

begin

#147

Gel'IAN, A.B

To

GEL'MAN, A. B.

GEL'MAN, A. B. - "Mineral nutrition and the mineral content of milk in feeding high-yield cows according to the system used at the Vologda Experimental Animal Husbandry Station". Leningrad, 1954. Min Higher Education USSR. Leningrad Agricultural Inst. (Dissertation for the degree of Candidate of Agricultural Sciences).

SO: Knizhnaya Letopis' №. 46, 12 November 1955. Moscow

BC

$a \cdot 3$

Electrolytic Compounds of platinum. A. ULRICH
 (Inst. Phys., Leopoldina State Univ., 1908, 2, No. 2,
 8-67). PbCl_4 is passed through an K_3PbCl_6 for
 15 days at room temperature, and an $[\text{Pt}(\text{C}_2\text{H}_5)_2\text{Cl}]_2$ is added,
 when $[\text{Pt}(\text{C}_2\text{H}_5)_2\text{Cl}]_2\text{PbCl}_4$ is formed. This reacts
 with K_3PbCl_6 to yield $\text{K}_2\text{Pt}(\text{C}_2\text{H}_5)_2\text{Cl}_2\text{H}_2\text{O}$ (I),
 identified with that obtained by fusion from Na_3PbCl_6 and
 PtCl_4 . $[\text{Pt}(\text{C}_2\text{H}_5)_2\text{Cl}]_2\text{H}_2\text{O}$ reacts with HCl to
 afford $\text{H}_2\text{Pt}(\text{C}_2\text{H}_5)_2\text{Cl}_2$, and was $\text{CH}(\text{NH}_2)_2$ (II) to
 give $\text{PtCl}_2\text{N}(II)$ (III), remaining in the cis configuration.
 An estimated prep. of the trans-isomeride by Jorgens-
 son's method was unsuccessful. (II) in dil. HCl and
 $\text{C}_2\text{H}_5\text{N}$ yield $[\text{Pt}(\text{C}_2\text{H}_5)_2\text{N}(\text{C}_2\text{H}_5)_2\text{Cl}]$ (IV), converted
 by HCl into $[\text{Pt}(\text{C}_2\text{H}_5)_2\text{N}(\text{C}_2\text{H}_5)_2\text{Cl}]_2$ by (II) into
 (III), and by action of $\text{C}_2\text{H}_5\text{N}$ has been trans-
 $[\text{Pt}(\text{C}_2\text{H}_5)_2\text{N}(\text{C}_2\text{H}_5)_2\text{Cl}]_2$ (I), and $[\text{Pt}(\text{C}_2\text{H}_5)_2\text{N}]_2\text{Cl}_2$ give
 $[\text{Pt}(\text{C}_2\text{H}_5)_2\text{N}(\text{C}_2\text{H}_5)_2\text{Cl}_2\text{H}_2\text{O}$. The salts
 $[\text{Pt}(\text{C}_2\text{H}_5)_2\text{N}(\text{C}_2\text{H}_5)_2\text{Cl}_2\text{H}_2\text{O}$ and
 $[\text{Pt}(\text{C}_2\text{H}_5)_2\text{N}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ are described. The stability
 of some of the salts $[\text{Pt}(\text{C}_2\text{H}_5)_2\text{N}_2\text{X}_2]$ rises in the series
 $\text{X} = (\text{II}) < \text{H}_2\text{O} < \text{C}_2\text{H}_5\text{N} < \text{CH}_2\text{NH}_2 < \text{CH}_2=\text{NH}_2$, and $\text{X} =$
 $\text{CH}_2=\text{NH}_2 < \text{CH}_2=\text{NH} < \text{C}_2\text{H}_5 < \text{CH}_2=\text{CH}_2 < \text{Cl}$. R. T.

AMERICAN METALLURGICAL LITERATURE CLASSIFICATION

APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2"

BC

1-3

Isomerisation of esterified compounds of platinum. I. I. TROKHIMOV and A. D. GOLIKOV. (Compt. rend. Acad. Sci. U.R.S.S., 1956, 4, 181-184).—By treating K_2PtCl_4 first with $\text{C}_2\text{H}_5\text{OH}$ and then with NH_3 or $\text{C}_2\text{H}_5\text{NH}_2$ ($\text{K}_2\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_2\text{Cl}_2$) is formed, apparently at a very high rate. A by-product was obtained by decomposing $\text{C}_2\text{H}_5\text{OH}$ at a ratio of a 2:1 ($\text{Pt}:\text{C}_2\text{H}_5\text{OH}$) ($\text{M} = 0.01$). These results are ascribed to the strong influence of $\text{C}_2\text{H}_5\text{O}^-$. B. C. R.

AM-314 METALLURGICAL LITERATURE CLASSIFICATION

APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2"

BL

R-1

Solvolysis complexes of platinum. I. I.
 T. S. HUMPHREY and A. D. GOMBERG (Ann. Berl. Platin., 1927, 20, 77-121).— PtCl_4 (I) in 3-5% HCl and C_2H_4 react at room temp. as follows (X = Cl, Br):
 (I) + $\text{C}_2\text{H}_4 \rightarrow \text{K}[\text{Pt}(\text{C}_2\text{H}_4\text{X}_2)]$ (II) + KCl . (III) reacts with $[\text{Pt}(\text{C}_2\text{H}_4\text{X}_2)]$ to give $[\text{Pt}(\text{C}_2\text{H}_4\text{M}_2\text{X}_2)]$ (M = NH_3 , $\text{C}_2\text{H}_5\text{N}$), and with M to afford the compound $[\text{Pt}(\text{C}_2\text{H}_4\text{M}_2\text{X}_2)]$. The equilibrium $[\text{Pt}(\text{C}_2\text{H}_4\text{M}_2\text{X}_2)]$ is shown to exist, and the products are isolated and described. The C_2H_4 complexes behave analogously to other Pt complexes; they are stable in dry air, and in light, but are instantly decomposed by heating or alkaline aq. solutions, with precipitation of Pt. The stability of the complexes rises in the series M = $\text{C}_2\text{H}_5\text{N}$ < NH_3 < $\text{C}_2\text{H}_4\text{N}$ < ammonia, and X = Cl < C_2H_4 < NO_2 < I < Br < Cl. Attempts to determine the configuration of the complexes were unsuccessful, owing to their instability.
 R. T.

AMERICAN METALLURGICAL LITERATURE CLASSIFICATION

SEARCHED

SERIALIZED

INDEXED

FILED

SEARCHED

SERIALIZED

INDEXED

FILED

三

A-1

Compounds of platinum with unsaturated hydrocarbons of the ethylene series. A. D. GELMAN (Compt. rend. Acad. Sci. U.R.S.S., 1937, 10, 331-334; cf. A., 1937, 11, 84).—Replacing Cl by Br, or C_6H_5 by propylene, isobutylene, or styrene, prop. and properties are given for further members of the complex type: $[C_6H_5XPtCl_3]$ where $X = NH_2$ or C_6H_5N . As with the chlorides, *trans*-forms are obtained from Zeiss type salts, *cis*- from Coss type. $[C_6H_5XPtCl_3]$ with KBr yield the bromides. The chlorides are inter-replaceable, showing residual affinities in the order $C_6H_5 > C_6H_6 > C_6H_4$ or C_6H_2 (cf. A., 1938, 1068). $[C_6H_5NH_2PtCl_3]$ when boiled with HCl yields Coss salt, showing elimination of C_6H_5 to be the primary reaction. The results confirm the *trans*-influence in the inner shell of the unsaturated mols.

APPENDIX METALLURGICAL LITERATURE CLASSIFICATION

APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2"

The isomerism of ethylene chloride compounds of platinum. I. I. Chernyaev and Anna D. Hoffman. *J. Russ. Phys. Chem. Soc.*, 18, 8, 38, No. 13, 5-12 (1906); cf. *C. A.* 33, 1437. When K_3PtCl_6 is treated with C_2H_2 and then NH_3 , $trans$ - $PCl_2H_2Cl_2NH_3$ (I) is formed. When NH_3 [PtCl₆] is treated with C_2H_2 , only the *cis* isomer can be formed, since the Cl opposite the NH_3 is strongly held by the *trans* effect. Actually, a yield of 70% of the *cis* isomer (II) of I is obtained. II decomposes, and deposits a Pt mirror after 5-6 min. in boiling H_2O , gives a ppt. with $AgNO_3$ and reacts with $CS-NH_3$ to form $[Pt(CS-NH_3)_2]Cl_6$. Its solv. at 25° is 0.233 g. per 100 cc. H_2O and 0.129 g. per 100 cc. $EtOH$. In an analogous way, $pytH_3$ [PtCl₆] and C_2H_2 give 50% $C_2H_2Cl_2PtCl_6$, decomposing about 160°, which has properties similar to those of II. Its solv. at 25° is 0.073 g. per 100 cc. H_2O and 0.053 g. per 100 cc. 90% $EtOH$. When II is dissolved in NH_3OH , the C_2H_2 is replaced by NH_3 . Thus, when C_2H_2 is added to a Pt compd. contg. an amine in the inner sphere, a *cis* compd. is formed, but if the amine is added to a Pt compd. with C_2H_2 in the inner sphere, the *trans* isomer results. H. M. Lester.

H. M. Levenson

APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2"

ca

Compounds of platinum and carbon monoxide. Anna D. Heimann and M. Baumann. *Compt. rend. acad. URSS*, 1938, 6(1), 615-618 (in English), cf. C. A. 32, 2881. II. and II. prep'd. the following compds. PtCl_3CO , $\text{PtCl}_3\text{C}_2\text{O}$ and $2\text{PtCl}_3\text{CO}$ previously described by Pullinger (*Ber.* 24, 2293 (1891)). They also prep'd. $\text{PtCl}_3\text{CO}2\text{NH}_3$, $\text{PtCl}_32\text{CO}2\text{NH}_3$ and $\text{PtCl}_3\text{C}_2\text{O}2\text{NH}_3$ by passing NH_3 and C_2O into CCl_4 solns. of the above-mentioned compds. The first mentioned group of compds. was prep'd. by the action of CO for 7-14 days at room temp. on a soln. of $\text{K}[\text{PtCl}_3]$ chloroplatinate. The color of the solns. gradually turned yellow and a cherry-red film formed at the surface. Addn. of an an. pyridine (Py) dropwise to the greenish-yellow filtrate which probably contained $\text{K}[\text{PtCOCl}_3]$ yielded a yellow ppt. according to the following equation: $\text{Me}_3\text{PtCOCl}_3 + \text{Py} \rightarrow (\text{PtCO}\text{Py})_3$.

MeCl. Reppin, of the crude product from a HCl soln. yielded a pure product of the compnd. indicated by formula in the equation. The yield is 30.4% theory and 31.4% act. In the ordinary method accounted for only 6.1% Cl act. However, when the substance was slowly reduced by Hg in acetate soln. 17.41% Cl was obtained (theoretical $\text{Cl} = 19.03\%$). PtCOPyCl_3 is lemon-yellow in color and is decomposed by Hg into PtCl_3 , $\text{C}_2\text{H}_5\text{N}$ and HCl . Its solv. in RtOH at 25° is 0.069 g. per 100 cc. and it melts with decompo. at 127-129 $^\circ$. It dissolves in dS- HCl and evapn. of the soln. yields crystals analyzing $\text{PtCl}_3(\text{PtCOCl}_3)$ and is identical with the compnd. described by Mylius and Loevner (*Ber.* 24, 2424 (1891)). Addn. of

CH_3N gives rise to a ppt. of the original substance $\text{PtCO}_2\text{PyCl}_3$. Thus, by analogy with the behavior of the $\text{C}_2\text{H}_5\text{N}$ -type compnd., the latter substance exists in the *trans* form $\text{Cl}=\text{Pt}=\text{C}_2\text{H}_5\text{N}$.

Cl $\text{Pt}=\text{C}_2\text{H}_5\text{N}$ The formation of the resp. *cis* isomer.

when a soln. of Kow's salt is treated with CO (process that $\text{C}_2\text{H}_5\text{N}$ and C_2O compds. of Pt are perfectly analogous to each other), Kow's Py salt yielded too small a quantity of the substance for investigation. With Kow's NH_3 salt, beautiful pale-yellow crystals of $(\text{PtNH}_3\text{ClCOCl})_3$ sept. after 6-10 days according to the equation: $\text{NH}_3[\text{PtNH}_3\text{Cl}_3] + \text{CO} \rightarrow \text{NH}_3\text{Cl} + (\text{PtNH}_3\text{ClCOCl})_3$. This reaction is very sensitive to temp.; normally it occurs only within the limits 11-14 $^\circ$. This substance presented no difficulty in its detn. of Cl content and according to the conditions of its prepn. (Cheruvayev and Heimann, *C. A.* 31, 2541) it has the *cis* form. It differs very markedly from the previously described substance, melting with decompo. at 180-185 $^\circ$; solv. in RtOH , 0.023 g. in 100 cc. soln. Thus, it has been established that CO just as C_2O and its homologs has a high *trans* influence on the complex. On this basis the *cis* and *trans* carbonyl-amino-dihalide of Pt having a compnd. $(\text{PtNH}_3\text{COCl})_3$ form have been prep'd. An attempt has been made to explain the high *trans* influence of CO and also the *trans* influence of $\text{C}_2\text{H}_5\text{N}$ and NO_2 through the fact that the C and N atoms are unsat.

W. A. Cook

42

Stability of substituted ethylene hydrocarbons. Anne L. Heilmann. *Compt. rend. acad. sci. U. R. S. S.* 20, 35; 101 (1938) (in English).—The stability decreases according to the sequence: styrene, $C_6H_5CH_2$, $C_6H_5CH_2$, C_6H_5 . CO has a greater stability than any of these. Greer M. Evans

ASA-SEA METALLURGICAL LITERATURE CLASSIFICATION

APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2"

Compounds of phenylmagnesium bromide with ethylbenzene, hydroquinone, and α -methylbenzyl alcohol (Ann. Soc. Polon. Mat., 1939, No. 32, 24-27; $\text{C}_6\text{H}_5\text{CH}_2\text{MgBr}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr}$ give compounds of this type: $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{MgBr}$, converted by e.g. NH_4^+ or $\text{C}_6\text{H}_5\text{CH}_2\text{MgBr}$ into

[$\text{PdCl}_2(\text{C}_6\text{H}_5\text{CH}_2)_2$] or [$\text{PdCl}_2(\text{C}_6\text{H}_5)_2\text{NH}_2\text{CH}_2\text{CH}_3$] ($\text{B} = \text{Me, Et, Ph}$); [$\text{PdCl}_2(\text{C}_6\text{H}_5)_2\text{NH}_2\text{CH}_2\text{CH}_3$] is a by-product in the case of $\text{CH}_3\text{PdCl}_2\text{NH}_2$; $\text{PdCl}_2(\text{PdCl}_2\text{NH}_2)_2$ and $\text{C}_6\text{H}_5\text{CH}_2\text{PdCl}_2$ afford the cis- and trans-[$\text{Pd}(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Cl}_2$]; cis- and trans-[$\text{Pd}(\text{C}_6\text{H}_5)_2\text{Cl}_2$] are prepared analogously. R. T.

R. 1

330-334 METALLURGICAL LITERATURE SURVEY

APPROVED FOR RELEASE: 08/31/2001

CTA-RDP86-00513R000514710001-2"

6
C +

ethylene nitrochloride of platinum. Anna D. Lippman and J. H. Luyk. *Ann. Soctet. Platin.* *1938* p77 (U. S. S. R.) No. 16, 29 31 (1939). $[(C_2H_5)_2PtCl_2]$ is best prep'd. by refluxing Na_2PtCl_6 for 6-8 hrs. with an excess of H_2O_2 and adding KCl . Excess K_2PtCl_6 ppts. and the filtrate is evap'd. in a vacuum until crystals begin. The salt can be purified by reaction with pyridine and regeneration with HCl . When 1 mol. of this salt reacts with 2 mol. of $NaNO_2$, $CaCO_3$ splits out and $Na_2Pt(NO_2)_2Cl_2$ is formed. If the proportions are not 1:1, the product is $Na_2Pt(C_2H_5NO_2)_2$, which is very sol., but reacts with $(NH_4)_2PtCl_6$ to give $[(NH_4)_2Pt(C_2H_5NO_2)_2Cl_2]$. The C_2H_5 and NO_2 groups are in the trans position in spite of the strong labilizing effect which each exerts. However, owing to this, the compd. reacts with pyridine to form $(PtC_2H_5)_2Cl_2$. Attempts to prep. a nonelectrolyte congl. C_2H_5 and NO_2 by treatment of $[(PtNH_3)_2Cl_2]$ with $NaNO_2$, or of $Na_2Pt(C_2H_5NO_2)_2$ with C_2H_5 were unsuccessful. Compds. of C_2H_5 or C_2H_5 with $Na_2H_2O_2$, $Co(NH_3)_4Cl_2$, or $Ni(CN)_4Cl_2$ could not be obtained. H. M. Lester

PROCESSES AND PROPERTIES AND

BC

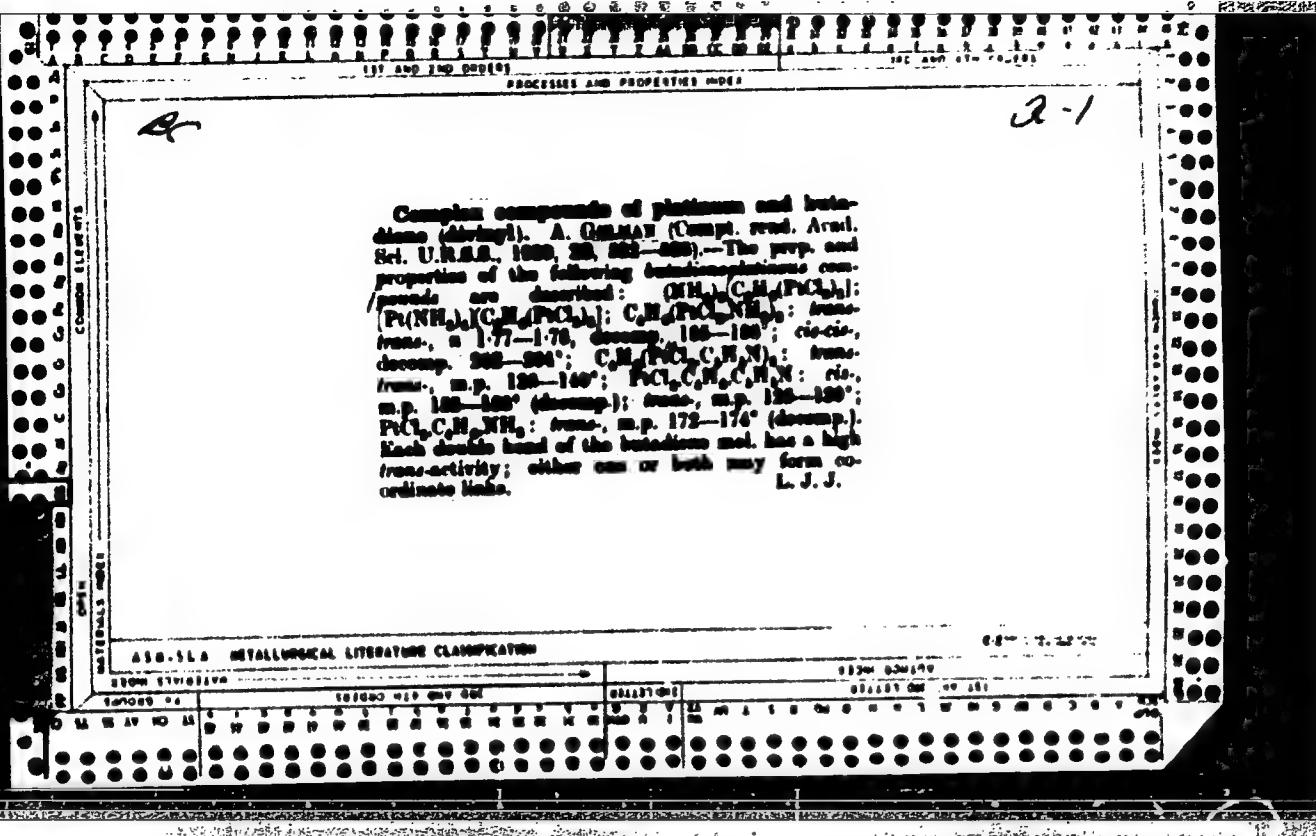
a-1

Mixed platinum chlorobisimides possessing a cis-configuration. A. GOLDBECK (Compt. rend. Acad. Sci. U.R.S.S., 1929, 22, 107-110).—Unlike the case previously recorded (Timchenko and Gol'dman, A., 1928, I, 94), introduction of NH_2 into $\text{NH}_2[\text{Pt}(\text{C}_2\text{H}_5)_2\text{Cl}_2]$ and $\text{C}_6\text{H}_5\text{NH}_2$ into $\text{NH}_2[\text{Pt}(\text{NH}_2)_2\text{Cl}_2]$ leads in each case to the $\text{NH}_2[\text{Pt}(\text{NH}_2)_2\text{C}_6\text{H}_5\text{N}_2\text{H}_2]$ (conductance at 20° measured), which with aq. NH_3 gives $\text{NH}_2[\text{Pt}(\text{NH}_2)_2\text{C}_6\text{H}_5\text{N}_2\text{H}_2]$ with Cl_2 followed by $\text{C}_6\text{H}_5\text{NH}_2$ yields $\text{NH}_2[\text{Pt}(\text{C}_6\text{H}_5\text{NH}_2)_2\text{Cl}_2]$, and with $\text{C}_6\text{H}_5\text{NH}_2$ gives $\text{PtCl}(\text{C}_6\text{H}_5\text{NH}_2)_2$ which with K_2PtCl_6 affords $\text{Pt}(\text{C}_6\text{H}_5\text{NH}_2)_2\text{PtCl}_6$. F. R. G.

130.3.8 METALLURGICAL LITERATURE CLASSIFICATION

APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2"



The theory of complex compounds. Anna L. Hickman (Compt. rend. acad. sci. U. R. S. S. 24, 549-1939) (in English).—The behavior of C_6H_5CO and NO in Pt coordination compds. is readily explained by the assumption of high *trans* influence (Chernyshev, *C.* 4, 23, 216), whereby the Pt atoms first as an electron donor to the activated C_6H_5CO or NO and then becomes an acceptor, this results in the formation of a 4-electron covalent bond with unsatd. molos. are formed in the only by bivalent Pt , and generally by metals in the lowest stage of oxidation. Only one unsatd. mol. of high *trans* influence can become a part of the complex and it is easily displaced by excess of NH_3 or pyridine. Two or three mol. of thera can enter the complex since it is an electron donor only and can give four electrons for common use.

Digitized by srujanika@gmail.com

APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2"

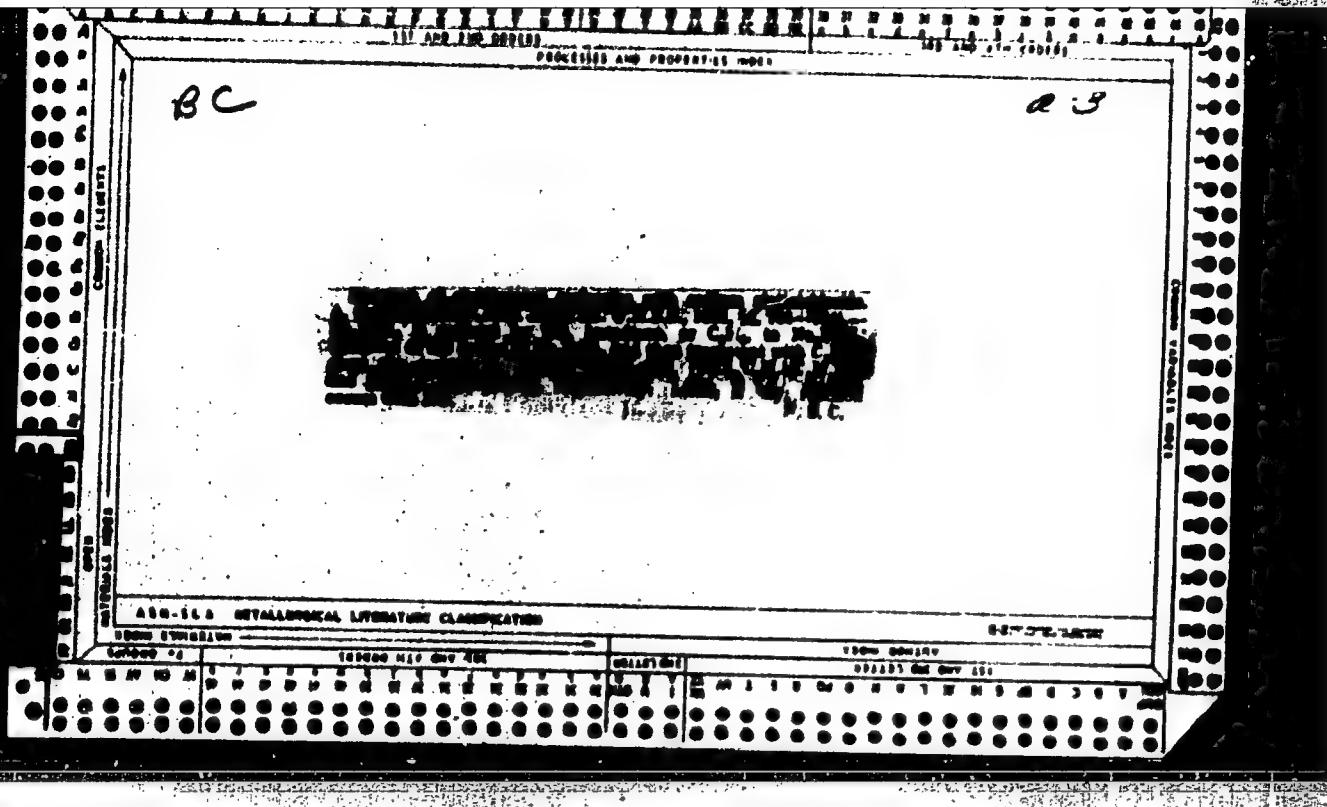
RECORDED AND INDEXED 8-1-66
6

Nitroaryl compounds of platinum. A. D. Hellman and
A. P. Atakumova. *Comp. rend. acad. us. U. R. S. S.* 24:
748-51 (1949); in English. On allowing a satd. soln. of
K or NH₃ chloroplatinate to stand 3-4 days in a N₂O atm. a
green soln. (I) formed, apparently owing the ion Pt⁺
N₂OCl₆⁻. Addn. of [Pt(NH₃)₆]²⁺ soln. to I gave a red-
dish gray ppt. of [Pt(NH₃)₅N₂OCl₆]₂. Adding pyridine
to I gave an immediate ppt. of PtN₂O₂Cl₆ (II) (green).
Dissolved in pyridine, II gave a yellow ppt. of PtPy₂Cl₆
which reacted with thiourea to give *trans*-PtPy₂Cl₆
Hence II has a trans configuration. N₂O does not react
with chloroplatinate. A. D. Allen

"APPROVED FOR RELEASE: 08/31/2001

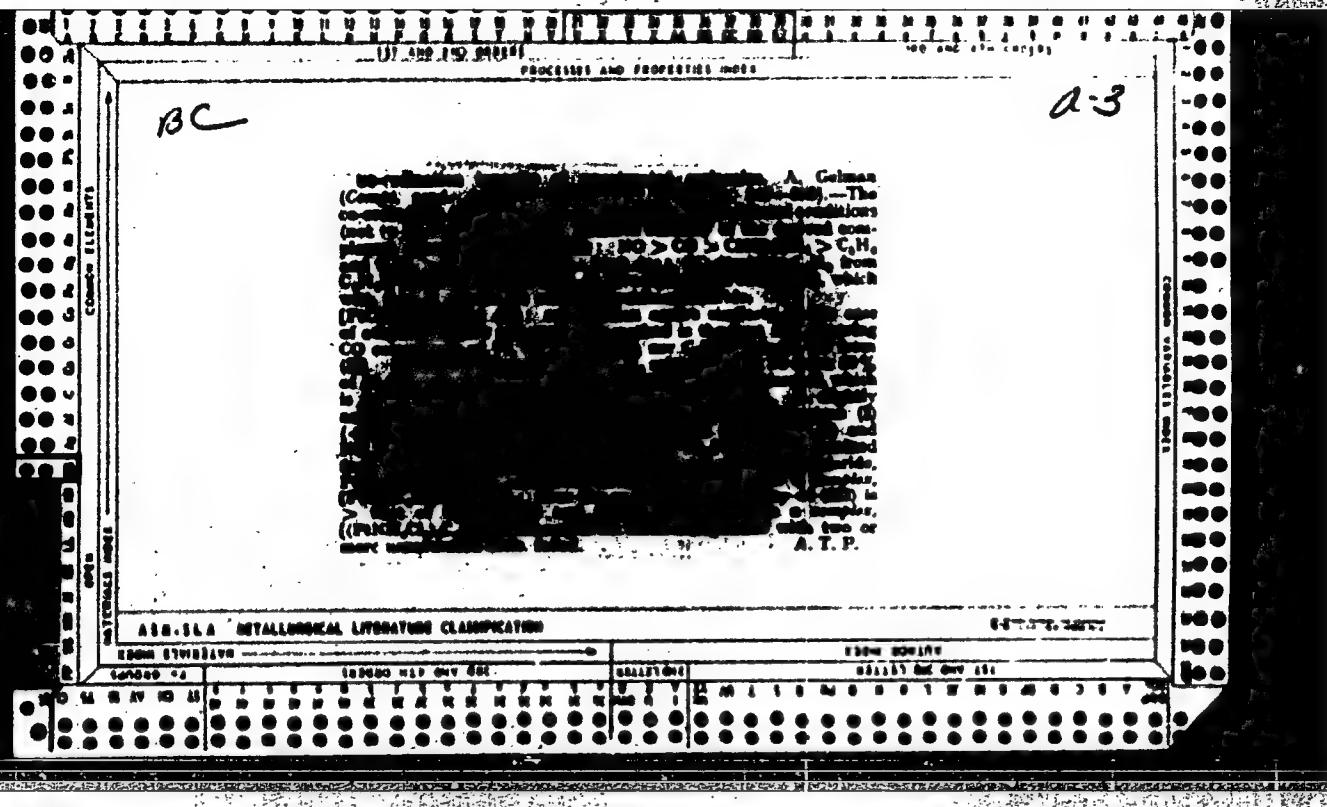
CIA-RDP86-00513R000514710001-2

41 46528 65



APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2"



Valency of platinum in ethylene complex compounds. A. D. Il'guman and D. I. Kyzichikov. *Compt. rend. acad. sci. U. R. S. S.* 33, 1614 (1941). By subjecting Conen's salt, $\text{NH}_4[\text{Pt}(\text{NH}_3)_6\text{Cl}_4]$, and Zeise's salt of the type $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)_6\text{Cl}_3]$ to electrometric oxidative titration with KMnO_4 in acid soln., establish the quadrivalence of Pt in the latter. I, in which Pt is bivalent, is oxidized normally and a jump in the potential is observed at the transition point. With II the initial potential of the salt, is 650-700 mv., which is characteristic of Pt (IV) compds., and no oxidation occurs.

J. C. Lo Cicero

APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2"

Components of palladium with carbon monoxide. A. Gelman and E. Meilach (Compt. rend. Acad. Sci. U.R.S.S., 1942, 50, 171-174).-- By passage of CO for several days through $(NH_4)_2PdCl_4$ in conc. HCl the compound obtained is not NH_4PdCl_3CO but $NH_4PdCl_2(CO)$. By metathesis reactions with $[P(NH_3)_4]Cl_2$ and with $(CH_3)_3NH_2Cl$, the compounds $[P(NH_3)_4]PdCl_2CuCl_2$ and $(CH_3)_3NH_2PdCl_2CO$ have been isolated. The structure of these compounds is discussed in terms of the co-ordination theory, and formulas are advanced on the assumption that the compounds are dimerides containing the ion

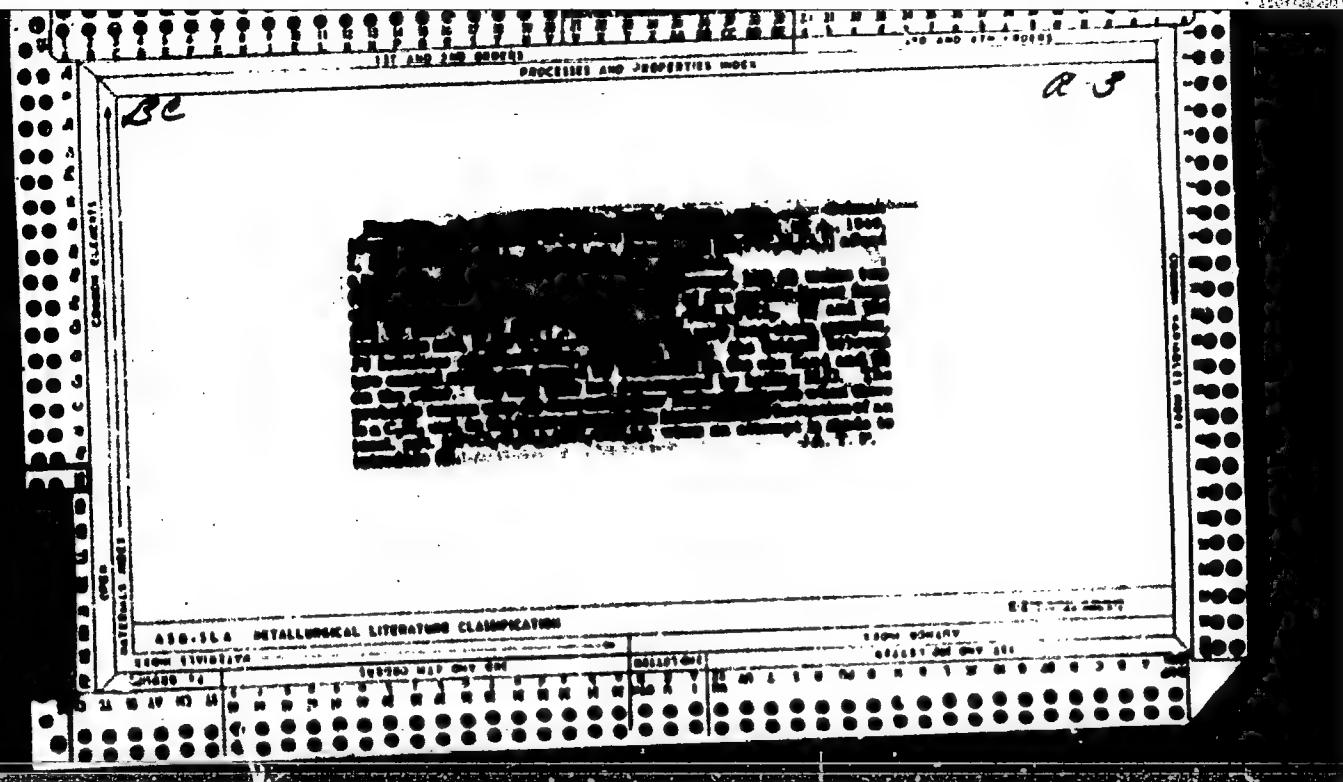
$$\left[\begin{array}{c} Cl \\ | \\ Pd \\ | \\ CO \\ | \\ Cl \end{array} \right] \left[\begin{array}{c} Cl \\ | \\ Pd \\ | \\ CO \\ | \\ Cl \end{array} \right]$$

The instability of the IV carbonyl halides probably causes Pd to be tervalent in these compounds.

J. O'M.-R.

"APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2



APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2"

150

A1

2

Synthesis of octahedral complexes of platinum with four different substituted groups in the inner sphere. A. Gelman (Compt. rend. Acad. Sci. U.R.S.S., 1943, 58, 510-513). The geometrical isomers $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{Cl} > \text{Pt} < \text{Br}$ (I) and $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{C} > \text{Pt} < \text{NH}_3$ (II) have the following properties: (I), greenish yellow prismatic crystals, $n_D^{20} 1.783$, $n_D^{20} 1.788$, insol. in cold HCl, decomposed by cold AgNO_3 ; (II), yellow crystals, $n_D^{20} 1.713$, $n_D^{20} 1.708$, sol. in cold HCl giving $\text{NH}_3[\text{Pt}(\text{C}_6\text{H}_5)_2\text{Cl}_2]$, giving a very feeble opalescence with cold AgNO_3 . Attempts to obtain the anion $[\text{Pt}(\text{C}_6\text{H}_5)_2\text{ClBr}]^-$ led to displacement of $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{C}$ from the complex. L. J. J.

C6H5C6H4Cl

ALB-1000 METALLURGICAL LITERATURE CLASSIFICATION

25

183. Complex Compounds of Platinum with Unsaturated Molecules. (In Russian.) Anna Gglman (Nikitina) 100 pages. 1945. Academy of Sciences of U.S.S.R. Institute of General and Inorganic Chemistry, Moscow.

After a short literature review of the complex ethylene compounds of platinum, a number of these reactions are investigated in order to test the validity of a theory advanced by Tschugaeff and others. Finally, the author proposes a new theory concerning reactions of unsaturated molecules with platinum. 113 ref.

Compounds of platinum with carbon monoxide. A-D.
 Gel'man, *Acta scientiarum platinum*, *Inst. chim. SSSR* (U.S.S.R.) 10, 30-40 (1945) (in Russian).—Solvn. of K- or NH₄ chloroplatinate(II), kept in contact with CO at room temp. for 7-14 days, formed gradually, besides a small amt. of a cherry red Pt config. sediment, a green-yellow filtrate from which dropwise addn. of pyridine (*py*) (under const. cooling with ice water) pptd. a yellow solid according to K[Pt(CO)Cl]₃ + *py* = KCl + [Pt(CO)₃*py*]₂ (I) with a yield of 30 %. On decompr. with hot water, AgNO₃ ppts. only about 1% of the Cl in I; nearly theoretical ppts. of Cl is attained only after slow reduction with Mg in AcOH. The compnd. I m. 127-0° with decompr.; solv. in EtOH 0.070 g/100 ml. at 25%; from a soln. of I in HCl, evapn. yields *py*[Pt(CO)Cl]₂ (II) which is readily reconvereted into I by *py*. From the reversibility I \rightleftharpoons II, it follows that in I the two Cl must be *py* in trans positions relative to each other, CO trans to *py*.

HCl
 The analogy of the Pt-*py* compds. with the corresponding Pt-C₆H₅ complexes demonstrated by the reaction NH₄[Pt(NH₃)Cl]₃ + CO \rightarrow NH₄Cl + [Pt(NH₃)Cl(CO)] (III) occurring only within the narrow temp. limits 11-14°, no reaction at all occurs at 0°, at 21° only the cherry red sediment forms. III proves to be a cis compd. by the ready ppts. of all its Cl by AgNO₃ after decompr. with hot water and relatively fast decompr. by cold water, decompr. without m. 180.5°; solv. in EtOH 0.021 g/100 ml.; insol. in HCl; refractive index n_D 1.790, n_D 1.743, n_D 1.722, ν 2770. Consequently, replacement of NH₃ by *py* results in a change of configuration which alone can account for the considerable difference of the properties of I and III. From a concn. soln. of II, [Pt(NH₃)₂]Cl₂ (IV), a compnd. shown to be [Pt(NH₃)₂]Cl₂[PtCl₃] (Magnum green salt) + 2 K[Pt(CO)Cl]₃ and 2 K[Pt(CO)₃*py*]₂ + 2 *py* = 2 I + 2 KCl; yield in IV, after washing with ether and drying, 86.5%. Treatment of I with HBr gives *py*H[Pt(CO)Cl]₂.H₂O. The high trans influence of both Cl₂ and CO, which cannot be explained by a dipole moment effect, might be tentatively ascribed to the unsatn. of C; this is borne out by the absence of complex formation with satd. hydrocarbons, and is paralleled by the trans influence of the NO₂ group. N. Then

Compounds of platinum with nitrile oxide. A. B. Gel'man and Z. P. Maksimova. *Zhur. sovetsk. chern. i khim. prom. (USSR)* 18, 61 (1945) (in Russian).
 From air-free soln. of K or NH₄ chloroplatinate(II), kept in contact with NO at room temp., a red-brown ppt. begins to form after 10-12 hrs., and the pptn. is complete after 3-4 days. The compnd. ptd. was identified as K₂[Pt(NOC₂)₄] (I) by: (1) its reaction with Pt(NH₃)₄Cl₂ resulting in pptn. of [Pt(NH₃)₄]Pt(NOC₂)₄Cl₂ (II), confirmed by analysis and by the reaction II + K₂PtCl₆ \rightarrow [Pt(NH₃)₄]PtCl₆ (languid green salt) + 2K[Pt(NOC₂)₄] (yellow-gray filtrate); (2) pptn., by dropwise addn. of pyridine (py), of [Pt(NO(py)Cl)₄] (III), confirmed by analysis. In analogy with the corresponding CO compnd. (cf. the foregoing abstract), only about 1/3 of the Cl can be ptd. by AgNO₃ after decomps. of the complex; fusion with Na₂O yields only a little more precipitable Cl than reduction with Zn + H₂SO₄; the airt. is somewhat increased by previous oxidation with H₂O₂. Microscopic examn. shows the presence of 2 phases, one with $\sigma_{\text{d}} > 1.785$, $\text{no} > 1.630$, the other $\sigma_{\text{d}} > 1.785$, $\text{no} > 1.730$, $\text{no} > 1.678$. The compnd. III is light green; with warm HCl it reacts
 HCl
 reversibly according to III \rightleftharpoons py H[Pt(NOC₂)₄].

ASB-SEA METALLURGICAL LITERATURE CLASSIFICATION

SEL'MAN, A.

Complex compounds of platinum with acetylene derivatives. A. Sel'man, S. Bulkovets, and E. Melnikh. *Doklady Akad. Nauk S.S.R.* 66, 110-12 (1955); *Compt. rend. acad. sci. U.R.S.S.* 66, 106-6 (1948) (in English). A concn. soln. of K_2PtCl_6 was heated with 2,5-dimethyl-3-hexyne-2,5-diol (Uu) to form water-sol. $K_2[PtUuCl_6]$, which was not isolated but was treated with pyridine to form $[PtUuPyCl_6]$ (I), pptd. as an oil undergoing crystall. on cooling and scratching with a glass rod. Cryst. I m. 88-7° (open tube) and 101-1° (sealed tube), decomposes in hot water and reacts with thiourea to form $[PtUuSC(NH_2)_2]Cl_6$. The mol. wt. of I, dextr., cryoscopically in benzene, m.w. was 686.3 (calcd. 687.36). The properties of I suggest that it exists in the same conformation. J. W. Perry

ASH-51A METALLURGICAL LITERATURE CLASSIFICATION

GELMAN, R. D.

Ch. 41

The production of complex platinum compounds with ethylene in the cation. A. D. Chernyaev and B. A. Mel'nik. *Comp. rend. acad. sci. U.S.S.R.* 51, 207-R (1946); *cf. C.A. 37, 6870 (1943).* — A Pt compd. was prep'd. as follows: *cis*-[PtCl₂(C₂H₄)NH₃]⁺, by treatment with ArNO₂, gave a nitro-chloro compd., in which the low co-ordinational strength of the NO₂ group makes the mol. readily hydrolyzable: [PtCl(NO₂)NH₃(C₂H₄)] + H₂O → [PtCl(H₂O)NH₃(C₂H₄)] + NO₂⁻. This product did not crystallize well and was unstable, but when an equimol. amount of pyridine was present, [PtCl(C₅H₅N)NH₃(C₂H₄)]NO₂ was formed; snow-white, crystalline, very sol. in H₂O. On standing it gradually darkens and turns dirty gray. In soln. the introduction of Cl⁻ or Br⁻ reverses the reaction, giving I, in accordance with Chernyaev's rule A. S. Eastman *C.J. 30, (1989).*

CA

Theory and practice of complex compounds of platinum with unsaturated molecules. Anna Gel'man and E. A. Mel'nikh. *Inst. Selskogo Plast'ya i Drug. Blagorod. Metal., Inst. Obshchel i Neft. Khim., Akad. Nauk S.S.R.* (Ann. secteur platine, Inst. chim. gen.) No. 20, 21-41 (1947).—Bispyridine was added dropwise to an aq. soln. of $K[Pt(C_6H_5Cl)_2]$ forming instantaneously a faint yellow ppt. of $[Pt(C_6H_5Cl)_2]_2C_6H_5N_2$. In this reaction the $C_6H_5N_2$ did not close a ring; it acted as bridge between 2 Pt atoms. Pt bisvinyl chloride formed a compd. with $C_6H_5N_2$ in which Pt atoms were connected on one side by C_6H_5 and on the other by $C_6H_5N_2$. Attempts to form a Pt ethylene tribisole compd. Cl, Br, and I were unsuccessful. This is attributed to the facts that I is in the trans position to C_6H_5 and both Cl and Br compete on the same coordinate for a covalent link with Pt. From the NH salt of $Pt(NH_3)_2Cl_2$, the cis and trans isomers of $[PtCl_2BrNH_3Cl]$ were produced. The action of Cl⁻ on a salt soln. of $(NH_3)_2PtCl_2$ yielded $NH_3[PtCl_2Cl]$ (I). The correctness of this formula was confirmed by causing I to react with $[Pt(NH_3)_2]Cl_2$ and with ethylenediamine hydrochloride. The reaction products were $[Pt(NH_3)_2]_2[PtCl_2Cl]$ and $(Cl_2NH_3)_2[PtCl_2Cl]$, resp. The Pt ethanoyl chloride is assigned the structure



Expts. on pptg. Pd and Pt from pure solv., slimes, and filtrate solns. of Ni and Cu by reducing the noble metals with C_6H_5 gave satisfactory results. The nature of Pt and Pd complexes with ethylene compds. indicates that the complexes are not coordination compds. but rather covalent.

M. Bloch

GEL'MAN, A.

PA 58T12

10-41 3802

USSR/Chemistry - Platinum Compounds
Chemistry - Isomers

Jan 1947

"The Formation of the Third Isomer of Ethylene-Ammonia-Chloride-Bromide Platinum," A. Gel'man, Ye. Gorushkina, Inst Gen and Inorg Chem imeni N. S. Kurnakov, Acad Sci USSR, 3 pp

"Dok Akad Nauk SSSR, Nova Ser" Vol LV, No 1

Describes experiments in which it was found possible to synthesize third isomer of ethylene-ammonia-chloride-bromide platinum; possible only after forming a group of atoms with ethylene in a cation. Submitted by Academician I. I. Chernyayev, 3 Jul 1946.

58T12

GEL'MAN, A.

PA 6076

Chemistry - Platinum
Chemistry - Organic Compounds

Jul 1947

"Alkyl Compounds of Platinum," A. Gel'man, Ye. Gorushkina, Inst Gen Inorg Chem imeni N. S. Kurra-kov, Acad Sci USSR, 2 pp

"Dok Akad Nauk SSSR, Nova Ser" Vol LVII, No 1

Describes experiments which enabled authors to obtain complex metalorganic compounds of platinum with pyridine and ethylene diamine of type $[(CH_3)_2 PtJ_2P_2]$ and $[(CH_3)_2 PtJ_2E_2]$.

6076

CA

The production of alkyl compounds of platinum from Zeise's salt. Anna D. Gelman and R. A. Goroshina. Doklady Akad. Nauk S.S.R. 57, 259 (1947). Chem. Zentral. (Russian Zone Ed.) 1948, 1, 126. The Pt in the ethylene salts of Zeise is to be regarded as quadrivalent. Attempts to replace the C_{2}H_{4} by NMe_{2} , pyridine, NO_{2}^{-} , or CN^{-} have yielded compds. with bivalent Pt. The salt $\text{Me}_3\text{Pt}(\text{C}_2\text{H}_4)$ (in which the Pt is quadrivalent) was successfully prep'd. by the action of MeMgI on the Zeise salt, $\text{K}[\text{PtC}_{2}\text{H}_4\text{Cl}_3]$. The MeMgI was prep'd. from 3 g. $\text{Mg} + 30$ g. MgI in 50 cc. ether. C_{2}H_4 (100 cc.) was added, then 10 g. $\text{K}[\text{PtC}_{2}\text{H}_4\text{Cl}_3]$ in small portions, next HCl to dissolve the $\text{Mg}(\text{OH})_2$, and the compd. recryst. from hot C_{2}H_4 in the usual manner. Dextr. prep'd. in like manner were: $[\text{Me}_3\text{Pt}(\text{C}_2\text{H}_4\text{N})]$, $[\text{Me}_3\text{Pt}(\text{NMe}_2)]$, $[\text{PtMe}_2\text{SO}_4]$, and Me_3PtCl_2 . M. G. Mende

Inst. (Sov. Acad. Chem. Ind.) Moscow, RSFSR

GEL'MAN, A. D.

USSR/Chemistry - Platinum
Chemistry - Isomers

Rev 48

"Obtaining ($\text{H}_3\text{C}-\text{H}_2\text{NCIBrPt}$) in the Form of Three
Expanded Isomers", A. D. Gel'man, Ye. F. Karandasheva
I. N. Kosen, Inst. of Gen and Inorg Chem Acad. N. S.
Kurnakov, Acad Sci USSR, 4 pp

"Dok Ak Akad SSSR" Vol LXXX, No 1

Studied problem of obtaining three expanded isomers
of a complex compound of bivalent platinum with the
most typical intraspHERE substitutes (pyridine,
ammonia, chlorine, bromine), using I. I. Chernyaev's
method. Analyzed trans- and cis-isomers and tabulated
law.

61/4927

USSR/Chemistry - Platinum (Contd)

Rev 48

the properties of the three isomers. Submitted by
Acad I. I. Chernyaev 26 Jun 48.

61/4927

21425

GEL'IAN, A. D.; PUXHOVETS, N. I.; ILYIN, I. A.

Kompleksnye soedineniya platiny s proizvodnymi atsotilema.
Soodshch. i. Izvestiya Sektora Platiny i Druzhikh Dlagorod.
Metallov (In-t Odshchey i Neorgan. Khimii im. Kurnakova),
Vyp. 23, 1949, s. 84 - 86.

SC: Letopis' Zhurnal'nykh Statey, No. 29, Moskva, 1949

GEL'MIN, A.

21424

GEL'MIN, A. D.; i MEYLAKH, E. A.

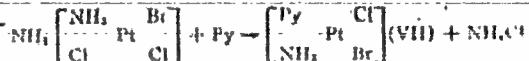
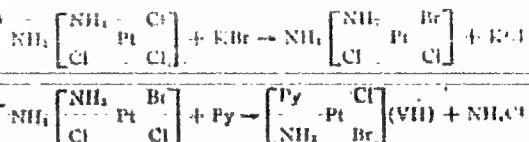
K Polucheniyu Kompleksnykh Soedineinny Platiny s Etilenom V
Kationa. Nvestiya Sektora Platiny k Drugikh Ilagorod.
Metallov (In - t Odshchey i Neorgah, Khimii im. Kurnakova),
Vyp. 23, 1949, s. 87 - 89.

SO: Letopis' Zhurnal'nykh Statey, No. 29, Moskva, 1949

GEL'MAN, R.D.

Production of chlorobromopyridinoaminoplatinum in its three isomeric forms. A. D. Orlitskii, G. E. Kurnikova, and L. N. Ezen. *Zhurnal Russkogo Platiny i Drajikha Blagorod. Metallov, Inst. Obrabotki Neorg. Khim. Akad. Nauk S.S.R.* No. 24, 60-71 (1949). — *cis*-[Pt(NH₃)₂Cl₂] (I) with C₆H₅N gives *cis*-[Pt(NH₃)₂PyCl₂] (II). II with (I) with C₆H₅N gives *cis*-[Pt(NH₃)₂PyCl₂] (III). III + AgNO₃ + HCl gives *trans*-[PtNH₃PyCl₂] (IV). IV + AgNO₃ + H₂O → [PtPyClNH₃H₂O]NO₃ (V) + AgCl. IV + KBr → [PtPyBrNH₃Cl] (V) + KNO₃ + H₂O or III + KBr → 2 V or IV + KBr → V + KCl. — *trans*-[PtPyBrNH₃] (VI) → 2 V or IV + KBr → V + KCl. Dissolve with heat 1.7 g. I in 3 ml. C₆H₅N and 50 ml. H₂O, cool, filter, add 30 ml. concd. HCl, and heat 3 hrs. under CO₂ atm. Cool, filter, and wash the ppt. until the filtrate is free of Cl⁻. Heat the filtrate with HCl and repeat the preceding operations. Combine with the 2 ppts., recrystallize III from hot H₂O, and dry over CaCl₂. By the first method dissolve 0.0310 g. of III in 60 ml. of H₂O. Add 0.2961 g. of AgNO₃ (in soln.), heat, keep in a dark place to settle out, and filter. To the filtrate add

0.2074 g. of KBr, filter, and recrystallize from hot H₂O. By the second method to a soln. of III add the required quantity of VI, heat to complete solution, and cool slowly. By the third method dissolve 0.0181 g. of III in 50 ml. of hot H₂O, add 0.2630 KBr, heat to 60°, stir for 4-5 hrs., and cool slowly. By the second method 0.5100 g. of VI in 10 ml. of hot H₂O, 11.4018 g. of KCl, heat for approx. 1 hr. at 80-90°, and cool slowly. Only the *cis* isomer (IV) is synthesized according to



To obtain the 2nd *cis* isomer dissolve 0.0310 g. of E₁Pt-PyCl₂ in a small vol. of slightly acidified H₂O, add 0.2039 g. of KBr. Heat over the water bath for 1-2 hrs., cool, and add dropwise with stirring to 10 ml. of H₂O, using 2-3 drops more than the required quantity for 2 hrs. at room temp. with occasional stirring, and filter.

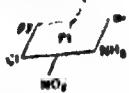
2/2 A. D. GELMAN, E. F. JAHN, V. V. PASHKOV
E. L. N. E. ESEN

filter, evap. the filtrate, and recrystallize at least twice from hot H_2O , to obtain $\left[\begin{smallmatrix} Pt & S \\ NH_3 & Cl \end{smallmatrix} \right] (VII)$, V, prismatic, lemon-yellow crystals, $n_D^{20} 1.776$, $n_D 1.770$, $n_D 1.567$, solv. in H_2O at $20^\circ 0.019$ g./100 g. of soln., decomposes approx. 224° , forms with thiourea $\left[\begin{smallmatrix} Pt & S \\ Thio & NH_3 \end{smallmatrix} \right] X_2$, VII, rhombic, pale-yellow crystal, $n_D 1.776$, $n_D 1.760$, $n_D 1.636$, solv. in H_2O 0.184 g./100 g. of soln., decomposes approx. 200° , forms $\left[\begin{smallmatrix} Thio & Thio \\ Pt & Thio \end{smallmatrix} \right] X_2$, VIII, light-yellow fine-cryst., $n_D 1.776$, $n_D 1.762$, $n_D 1.633$, solv. in H_2O 0.145 g./100 g. of soln., decomposes approx. 165° , forms $\left[\begin{smallmatrix} Thio & Thio \\ Thio & Pt \end{smallmatrix} \right] X_2$.

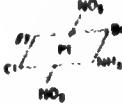
M. H. ch.

C7

Complex compounds of quadrivalent platinum with six different substituents in the inner sphere. A. B. G. Guseva and L. N. Ioven (N. B. Kurnakov Inst. (Chem. Fund. Chem. Acad. Nauk U.S.S.R., Moscow). Dobrolyubov Nauk S.S.S.R. 70, 603-8 (1950).—The



Isomer of $[\text{Pt}(\text{NH}_3)_5\text{Cl}] \text{Cl} (\text{Pt} = \text{C}_{12}\text{H}_{10})$ was syn-
thesized by first heating $[\text{Pt}(\text{NH}_3)_5\text{Cl}] \text{Cl}$ with HNO_3
which yielded



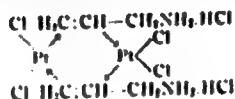
(II), bright-yellow, refractive indexes $n_1 = 1.782$, $n_2 = 1.73$,
(II), $0.013 \text{ g.}/10 \text{ g.}$ pale, at 100° , stable up to 200° ,
the soln. of the salt, out of Pt to a boiling soln. of II,
a dark-brown subl. was formed which, on cooling to room
temp., gave a ppt. of dark-brown crystals, $n_1 = 1.763$, with
yellowish to black phenanthrene, III, 341° (compd.), pale.
In II (2), $0.014 \text{ g.}/10 \text{ g.}$ pale, at 20° , easily red. to ab. The
analysis corresponds to I.

1951

CH

6

Complex compounds of platinum with allylamine. A. D. Gel'man and L. N. Ester (N. S. Kurnakov Inst. Gen. and Inorg. Chem., Acad. Sci. U.S.S.R., Moscow). Doklady Akad. Nauk S.S.R. 77, 273-5 (1961).—Reaction of a neutral soln. of K_2PtCl_6 with $CH_2=CHCH_2NH_2$ (I) gives the salt $[PtCl_4]_2$ (II) dark-yellow, stable on heating with H_2O , sparingly sol., dissolving in NH_4OH with a reddish brown color. That soln. in NH_4OH , acidified with HCl , gives with K_2PtCl_6 a dirty-green ppt. of $[(NH_3)_2PtI_2]_2[PtCl_6]$. These reactions prove that in II, the double bond of I takes no part in the complex formation; I is bound to the Pt only by the NH_2 group. Addn. of I to the Pt atom through the double bond takes place on heating in an acid medium or on prolonged reaction at room temp. Thus, heating of strongly acid soln. of K_2PtCl_6 with I gives a golden-yellow soln., which on cooling ppts. golden-yellow crystals of a dimer $[Cl_2PtCl_2(CH_2=CHCH_2NH_2)_2HCl]_2$ (III); to this the structure



is assigned by analogy with C_6H_5 and $PhCH_2:CH_2$ compds. Heating with H_2O produces a Pt mirror; this indicates bonding through the double bond. Prolonged heating of III with 10% HCl gives the Zeise-type acid $H[Cl_2PtI_2HCl]$ (IV), which on careful neutralization with 5% $NaOH$ forms a canary-yellow ppt. of $[Cl_2PtI_2]$ (V), obviously a cyclic complex, $\left[\begin{array}{c} Cl \quad CH_2:CH \\ | \quad \quad \quad | \\ Cl \quad Pt \quad NH_2CH_2 \\ | \quad \quad \quad | \\ Cl \quad H_2C:CH-CH_2NH_2 \cdot HCl \end{array} \right]$, giving metallic Pt on boiling with H_2O . This structure is confirmed by the synthesis $NH_3[Cl_2PtCl_2]$ (Zeise's salt) + $1 HCl \rightarrow NH_3[Cl_2PtI_2HCl] + Cl_2H_2$ (evolved), followed by $NH_3[Cl_2PtI_2HCl] + NaOH \rightarrow V$. Then

1452

CA

6

Preparation of the three spatial isomers of platinum chlorodipyrromethane. A. D. Gel'man and B. P. Karandashev. *Doklady Akad. Nauk S.S.R.* 78, 177-80 (1961).—By Chernyaev's rules, synthesis of the *trans* isomer (T) of $[\text{Cl}(\text{NH}_3\text{Py})\text{Pt}]$ ($\text{Py} = \text{C}_6\text{H}_5\text{N}$) should be feasible through $[\text{Cl} \text{ Pt} \text{ NH}_3] + \text{KI} \rightarrow [\text{Py} \text{ Pt} \text{ NH}_3] + \text{KCl}$; the *cis*(I) isomer (CI) should be obtained through $\text{NH}_3 [\text{NH}_3 \text{ Pt} \text{ Cl}] \xrightarrow{\text{KI}} \text{NH}_3 [\text{Cl} \text{ Pt} \text{ Cl}] \xrightarrow{\text{KI}} [\text{NH}_3 \text{ Pt} \text{ Cl}]$, and the *cis* (II) isomer (CII) through $\text{K}[\text{Cl} \text{ Pt} \text{ Cl}] \xrightarrow{\text{KI}} [\text{Py} \text{ Pt} \text{ Cl}]$. These theoretically predicted paths of synthesis were confirmed experimentally. Reactions between $[\text{PyNH}_3\text{Pt}]$, 0.3-1.0 g., in suspension in 25-75 ml. H_2O , and KI (in 1% excess over the molar ratio) gave, on 1/10 molar, yellow-orange powders of T. A 0.2-1.0 g. sample of $[\text{NH}_3\text{PtNH}_3\text{Cl}]$ in 10-30 ml. hot alk., with the calcd. amt. of KI , changed from golden yellow to dark yellow; dropwise addition of the calcd. amt. of Py gave brown-yellow fine needles of CI. Addn. of the calcd. amt. of KI to $[\text{PyPtCl}_3]$ in hot alk. soln., followed by dropwise addition of 20% NH_3OH , gave yellow needles of CII. The properties of T, CI, and CII, are: refractive indices, $n_D > 1.700$, $n_D = 1.70$; $n_D > 1.702$, $n_D = 1.718$; and $n_D > 1.702$, $n_D = 1.720$, m.p. in H_2O at 20° , 0.018, 0.024, and 0.022 g./100 g. mass; decomps. temp. on heating in a crucible in air, 210, 150, and 170° ; reaction with $\text{C}_2(\text{NH}_3)_2$ (10) produces, resp., $[\text{Py} \text{ Pt} \text{ NH}_3] \text{X}_2$ (non-white), $[\text{Pt} \text{ NH}_3] \text{X}_2$ (yellow), and $[\text{Pt} \text{ NH}_3] \text{X}_2$ (yellow). N. Thus

1. GEL'VAN, A. D. and KARANDASHOVA, Ye. F.
2. USSR (600)
4. Platinum Organic Compounds
7. Reaction of triacidoaminoplatinates of potassium $K\left[PtNH_3Cl_2X\right]$ with pyridine,
Dokl. AN SSSR 87 No. 4, 1952.

9. Monthly List of Russian Accessions, Library of Congress, February 1953, Unclassified.

GEL'MAN, A.D.

GRINBERG, A.A. (Leningrad); BABAYEVA, A.V. (Moscow); YATSIMIRESKIY, K.B. (Ivanovo); GOREMYKIN, V.I. (Moscow); BOLIY, G.B. (Moscow); FIAL-KOV, Ya.A. (Kiyev); YAKSHIN, M.M. (Moscow); KEDROV, B.M. (Moscow); GEL'MAN, A.D. (Moscow); FEDOROV, I.A. (Moscow); MAKSYMUK, Ye.A. (Leningrad); VOL'KENSHTEYN, M.V. (Leningrad); ZHDANOV, G.S. (Moscow); PTITSYN, B.V. (Leningrad); ABLOV, A.V. (Kishinev); VOLSHTEYN, L.M. (Dnepropetrovsk); TROITSKAYA, A.D. (Kazan'); KLOCHKO, M.A. (Moscow); BABAYEVA, A.V.; TROTSKAYA, V.G. (Moscow); RUBINSHTEYN, A.M. (Moscow); CHECHYAYEV, I.I.; GRINBERG, A.A.; TANAHAYEV, I.V.

Explanation of the transeffect. Inv. Sekt. plat. i blag. met. no. 28:
56-126 '54.
(Compounds, Complex) (Platinum)

GEL'MAN, A.D.

Preparation of the coupling compounds of quinonoid dianthraquinone with all different types of electron donors and acceptors. Part I. Coupling with aromatic diamines, Part II. Coupling with aromatic diols, Part III. Coupling with aromatic dicarboxylic acids, Part IV. Coupling with aromatic dicarboxylic anhydrides, Part V. Coupling with aromatic diesters, Part VI. Coupling with aromatic diimides, Part VII. Coupling with aromatic diisocyanates, Part VIII. Coupling with aromatic diisothiocyanates, Part IX. Coupling with aromatic diesters, Part X. Coupling with aromatic diimides, Part XI. Coupling with aromatic diisocyanates, Part XII. Coupling with aromatic diisothiocyanates.

from the dichloride ($\text{pyNH}_2\text{CH}_2\text{PtCl}_2$) by treating it with NaNO_2 . — J. Reyer, Leich.

My
bro
MT

Gel'man, A.D.

Preparation of 2,2-dimethyl-2-phenylpropanoic acid derivative.
A.D. Gel'man and L.N. Erem', Proc. Acad. Sci. U.S.S.R.,
Ser. Chem. 107, 169-200 (1960) (Engl. translation).—See
C.A. 50, 183185.

Class

2

3

PM

DEV

Gel'man, A. D.

USSR/Inorganic Chemistry - Complex Compounds

C.

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4099

Author : Gel'man, A. D., Eosen, D.N.

Inst : Academy of Sciences USSR

Title : Preparation of Mitrodichloro-Monoammino Platooate of Potassium

Orig Pub : Dokl. AN SSSR, 1956, 107, No 6, 835-836

Abstract : To prepare crystalline $K\left[\text{PtNH}_3\text{ClNO}_2\text{Cl}\right]\cdot\text{H}_2\text{O}$ (I) 1 mole of NaNO_2 was added to a warm aqueous solution of $K\left[\text{PtNH}_3\text{Cl}_3\right]$ (II). By addition of $\left[\text{Pt}(\text{NH}_3)_4\right]\text{Cl}_2$ to the reaction mixture a yellowish-orange precipitate of $\left[\text{Pt}(\text{NH}_3)_4\right]\left[\text{PtNH}_3\text{ClNO}_2\text{Cl}\right]_2$ (III) was produced. Salt III was ground with water and there was added thereto a calculated amount of $K_2\left[\text{PtCl}_4\right]$. The Magnus salt that was formed was filtered off and the solution was evaporated at $50-60^\circ$ on a water bath. The residue was ground repeatedly with alcohol. Dried over CaCl_2 it

Card 1/2

- 15 -

GEL'MAN, A. D.

1/ The preparation of quadrivalent platinum complex compounds with five and six different substituents in the inner spheres of the trans and cis configurations. L. N. Eisen and A. D. Gel'man. Doklady Akad. Nauk S.S.R. 103, 651-654 (1955). *Zh. S.S.R. 108, Sect. Chem. Sci.* (English translation) (1956) - [PyNH₂ClNO₂Pt] was obtained by the interaction of [PyNH₂Cl₂Pt] with the same amt. of NaNO₂. To water suspension of the product, Br₂ was added dropwise, with a thorough agitation after each addn. The original mixt. changed through greenish-brown to brilliant yellow; the ppt. was filtered, analyzed, and its compn. was found to be [PyNH₂ClNO₂Br₂Pt] (I). One Br was replaced with I by adding KI to a suspension of I in water, the mixt. heated for 20-25 min. on the water bath, the mixt. cooled, filtered, and the ppt. recrystd. from hot alc. Its compn. was found to be [PyNH₂ClNO₂BrI₂Pt] (II). Its structure was confirmed by its method of prepn. and by its reac. \rightarrow to the tetravalent Pt compnd. [PyNO₂NH₂Cl₂Pt]. The tetravalent compnd. was obtained from the mixt. [PyNO₂NH₂ClBr₂Pt] by a similar oxidation with Br₂ and replacing one Br with I - [PyNO₂NH₂ClI₂Pt] \rightarrow [PyNO₂NH₂ClBrI₂Pt].

2/ [PyNO₂NH₂ClBrI₂Pt]. The compnd. obtained has the compn. of (II), but different phys. properties, therefore they are isomers. Structures are given for 3 stereoisomers of quadrivalent Pt complexes contg. six different ligands.

W. M. Sorenson

Inst.-Phys.-Chem., A.S. USSR

1. Compounds of platinum with dinitrogen and diethyldinitrogen
amide. A. D. L. Cram and R. E. Lutz, J. Am. Chem. Soc., 51, 1515
(1929). The reaction of $\text{PtCl}_4 \cdot 2\text{H}_2\text{O}$ with $\text{R}_2\text{N}-\text{NH}_2$ produces
a colorless diamine platinum salt, $[\text{Pt}(\text{R}_2\text{NH})_2\text{Cl}_2 \cdot \text{H}_2\text{O}]$, which
reacts with $\text{R}'\text{S}$ residues to give $[\text{Pt}(\text{R}_2\text{NH})_2\text{Cl}_2 \cdot \text{H}_2\text{O}]$ with
 HCl or the nitroso group is replaced by the $\text{R}'\text{S}$ element
of the $\text{A}'\text{R}'\text{S}$ group. $[\text{Pt}(\text{R}_2\text{NH})_2\text{Cl}_2 \cdot \text{H}_2\text{O}]$ reacts with
changes with loss of $\text{A}'\text{R}'\text{S}$ up to the point where
 $\text{R}'\text{S}$ leads to replacement of a chlorine atom by a $\text{R}'\text{S}$ group
by HCl . The final step is the replacement of the remaining
chlorine atom by $\text{R}'\text{S}$ group. Thus, $[\text{Pt}(\text{R}_2\text{NH})_2\text{Cl}_2 \cdot \text{H}_2\text{O}]$
($\text{PtCl}_2 \cdot 2\text{Me}_2\text{S}$) changes slowly in H_2O solution to a
yellow light opalescence slowly with Ag_2S ; in H_2O , does
not react with NH_3OH or pyridine, and with CSNH_2 forms
 $[\text{Pt}(\text{CSNH}_2)_2\text{Cl}_2]$ and the cis isomer, green-yellow,
 169° , sparingly sol. Immediately, however, a pt with
 AgNO_3 reacts with NH_3OH forming $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, while
with pyridine it forms $[\text{Pt}(\text{py})_2\text{Cl}_2]$, the same material
forms with $\text{CS}(\text{NH}_2)_2$ as above. The amt. of cis isomer can
be raised to 80-99% by addg. an excess of Cl^- (KCl) and
some 20-30% excess of $\text{R}'\text{S}$ to the reaction mixt.; heating
to 30° also tends to take the yield of the cis isomer.

he ein Ritter.
G. M. Knoblauch

APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2"

AUTHORS	Gelman A.D., Matorina N.N., Moskvin A.I.	89-10-4/36
TITLE	Determination of the Composition and Instability Constants of Pu^{+3} Oxalate Complexes.	
PERIODICAL	(Oprudeleniye sostava i konstant nestoykosti oksalatnykh kompleksnykh ionov Pu^{+3}) - Russian).	
ABSTRACT	Atomnaya Energiya, 1957, Vol 3, Nr 10, pp 308 - 313 (U.S.S.R.)	
	The solubility of $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ in aqueous $\text{K}_2\text{C}_2\text{O}_4$ -solution of the most various concentrations /0,01 - 2,4 Mol/l/ was measured at constant ionization of the solution and at a temperature of 20°C. Forming of Pu^{+3} complexes was proved and the following ion complexes were formed: $[\text{Pu}(\text{C}_2\text{O}_4)_2]^-$, $[\text{Pu}(\text{C}_2\text{O}_4)_3]^{-3}$ and $[\text{Pu}(\text{C}_2\text{O}_4)_4]^{-5}$ with the instability constants: $4,9 \cdot 10^{-10}$; $4,10 \cdot 10^{-10}$ and $11,9 \cdot 10^{-11}$ respectively. The solubility of $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ in an aqueous $(\text{NH}_4)_2\text{C}_2\text{O}_4$ -solution at an ammonium concentration of 0,07 - 0,7 mol/l at a temperature of 70°C was also measured. The following ion complexes with the instability constants were found:	
	$[\text{Pu}(\text{C}_2\text{O}_4)_2]^-$ $11,6 \cdot 10^{-9}$	
	$[\text{Pu}(\text{C}_2\text{O}_4)_3]^{-3}$ $5,6 \cdot 10^{-9}$	
	$[\text{Pu}(\text{C}_2\text{O}_4)_4]^{-5}$ $2,5 \cdot 10^{-9}$	
SUBMITTED	There are 4 figures, 3 tables and 7 Slavic references.	
AVAILABLE	January, 19, 1957	
Card 1/1	Library of Congress.	

SUBDIVIDED
AVAILABLE
Card 1/1

(Signature)

AUTHORS: Gel'man, A. D., Matorina, N. N. and
Moskvin, A. I.

20-1-23/42

TITLE: An Investigation of the Formation Conditions and of the
Stability of Complex Oxalate Compounds of Pu (III) in
Aqueous Solutions (Issledovaniye usloviy obrazovaniya i
prochnosti oksalatnykh kompleksnykh soyedineniy Pu (III)
v vodnykh rastvorakh).

PERIODICAL: Doklady AN SSSR, 1957, Vol. 117, Nr 1, pp. 88-91 (USSR)

ABSTRACT: From other publications it is well known, that Pu (III)
shows much less preference for the formation of complexes.
The authors studied the stability of solutions of oxalate,
carbonate, citrate and ethylene-diamine-tetra-acetate
complex compounds of Pu (III) against oxydation by the
oxygen of the air by spectral photometric methods. It
appears, that Khindmen was correct with his assumption,
that complex formation cannot cause a noticeable modifi-
cation of the absorption spectrum of Pu (III). After the
authors having established the conditions of the above-
mentioned stability, they approached the problem of the
determination of the composition and of the instability

Card 1/4

20-1-23/42

An Investigation of the Formation Conditions and of the
Stability of Complex Oxalate Compounds of Pu (III) in
Aqueous Solutions

constant of the complex ions of PU (III) with various complex constituents. Two methods were employed: a) the method of solubility (at pH~8) and b) the method of ion-exchange (at pH ~ 1'4 - 3'0). a) At first the solubility of $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ in aqueous solutions of $\text{K}_2\text{C}_2\text{O}_4$ at 20°C and at a constant ion density of the solution was determined. Pu (III) was protected against oxydation by a nitrogen jet. The plutonium contents of the solution were determined by radiometric measurements. The results are given in table 1, from which the composition and the general instability constants (reference 6) of the oxalate complex ions of Pu (III) were determined or computed, respectively. In the range of concentration of $\text{K}_2\text{C}_2\text{O}_4$ under investigation complex ions are formed (more exactly a relation between Pu (III) and the $\text{C}_2\text{O}_4^{2-}$ -ion): $[\text{Pu}(\text{C}_2\text{O}_4)_2]^{2-}$, $[\text{Pu}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{Pu}(\text{C}_2\text{O}_4)_4]^{5-}$, the total concentration instability constants

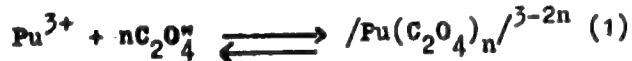
Card 2/4

An Investigation of the Formation Conditions and of the
Stability of Complex Oxalate Compounds of Pu (III) in
Aqueous Solutions

20-1-23/42

of which ("obshchiye kontsentratsionnyye konstanty nestoykosti") corresponding to $4.9 \cdot 10^{-10}$; $4.1 \cdot 10^{-10}$ and $1.2 \cdot 10^{-10}$, are equal. The dependence of the concentration of the ions in question on the concentration of the complex constituent is illustrated in figure 1.

In an analogous way the solubility of $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ in aqueous solutions of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in the range of concentration of the ammonium oxalate from 0'07 to 0'7 Mol/l at 70°C was determined (table 1). In this process complex ions of the same composition are formed, the total instability constants of which for $\text{Pu}_2(\text{C}_2\text{O}_4)_2$ $\sim 11.6 \cdot 10^{-9}$, for $[\text{Pu}(\text{C}_2\text{O}_4)_3]^{3-}$ $5.6 \cdot 10^{-9}$, and for $[\text{Pu}(\text{C}_2\text{O}_4)_4]^{5-}$ $2.5 \cdot 10^{-9}$ are equal. The heat of formation of the complex ions in the case of the reaction



Card 3/4 was also computed. It was found, that ΔQ equals 1300 Kcals

Finally, the distribution of Pu (III) between the 1 molar solution of NH_4Cl and of "cationite" KU-2 (reference 15) was determined with respect to the pH-value of the solution (table 2). There are 2 figures, 2 tables, 8 pages.

APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R000514710001-2

ASSOCIATION: Institute for Physical Chemistry AN USSR (Institut fizicheskoy khimii Akademii nauk SSSR)

PRESENTED: June 24, 1957, by I. I. Chernyayev, Academician

SUBMITTED: June 13, 1957

AVAILABLE: Library of Congress

Card 4/4

Gelman, A.D.

13-11-1
1-11-1
1-11-1

Coprecipitation of cerium by uranium(IV) oxalate. A. I. Kuznetsov and A. D. Gelman. *Zhur. Neorg. Khim.* 1, 1436-40 (1957).—The copptn. of microquantities of radioactive Ce⁴⁺ with the oxalate of U⁴⁺ was studied. Ce forms anomalous mixed crystals with the U oxalate. When the U compd. was pptd. without mixing, the Ce was carried down to a greater extent than that which corresponds to the equil. state and it does not obey the logarithmic law. In the system U(C₂O₄)₂-Ce(C₂O₄)₂ no lower limit was observed for the mixing, and the upper limit increases with an increase in the U concn. J. Rovtar Leach-

78-3-4-24/38

AUTHORS: Moskvin, A. I., Gel'man, A. D.

TITLE: Investigation of the Physico-Chemical Properties of Aqueous Solutions of Plutonium Oxalate (IV) and the Determination of Their Solubility Products (Issledovaniye fiziko-khimicheskikh svoystv vodnykh rastvorov oksalata plutoniya (IV) i opredeleniye yego proizvedeniya rastvorimosti)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 4, pp. 956-961 (USSR)

ABSTRACT: The solubility of plutonium-IV-oxalate in water and in the acids H_2SO_4 , HNO_3 and $HClO_4$ was determined.

Based on the solubility of plutonium-IV-oxalate, the determination of the pH-value and the electric conductivity of the saturated aqueous solutions of $Pu(C_2O_4)_2 \cdot 6 H_2O$ it was found that the aqueous solutions of plutonium-IV-oxalate have acidic properties. In the saturated aqueous solution of $Pu(C_2O_4)_2 \cdot 6 H_2O$ the hydrogen-ion concentration $[H^+] = 3.98 \cdot 10^{-8}$.

The dissociation constant of plutonium-IV-oxalate = $2.7 \cdot 10^{-5}$.

The solubility of $Pu(C_2O_4)_2 \cdot 6 H_2O$ decreases with the decrease of the pH-value of the solution. With an increase of the acid

Card 1/2

78-3-4-24/38

Investigation of the Physico-Chemical Properties of Aqueous Solutions of Plutonium Oxalate(IV) and the Determination of Their Solubility Products

concentration the solubility increases under the formation of complexes of Pu-IV with the anion of the corresponding acid. For the determination of the solubility product of $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{H}_2\text{O}$ a mixture of HNO_3 -(NH_4)₂ C_2O_4 was used. The solubility product amounts to $4 \cdot 10^{-22.4}$. This new method for the determination of the solubility products of difficultly soluble precipitates in acids is also used successfully in other systems, as for instance with $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{H}_2\text{O}$, $\text{UO}_2(\text{C}_2\text{O}_4)_2 \cdot 3 \text{H}_2\text{O}$, and others. There are 2 figures, 5 tables, and 12 references, all of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
(Institute for Physical Chemistry, AS USSR)

SUBMITTED: July 27, 1957

Card 2/2

OMEL'MAN, A.D.; METOD'YEVA, N.P.

Preparation of trivalent neptunium. Dokl. AN SSSR 117 no.2:225-226
(MIRA 11:3)
N '57.

1. Institut fizicheskoy khimii Akademii nauk SSSR. Predstavлено
академиком I.I. Chernyaevym.
(Neptunium)

AUTHORS: Ivanova, O. M., Gel'man, A. D.

78-3-6-9/30

TITLE: On the Amino Derivatives of Trimethyl Platinum
(Ob aminoproizvodnykh trimetilplatiny)PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 6,
pp. 1534-1546 (USSR)ABSTRACT: The properties of some organometallic compounds of platinum
were investigated and the synthesis of the amino derivatives
of trimethyl platinum was described. The following six mixed
organometallic compounds of platinum were synthesized:
$$(\text{CH}_3)_3\text{PtOCH}_3, (\text{CH}_3)_3\text{PtBr}, [\text{Pt}(\text{CH}_3)_3(\text{NH}_3)_3]\text{Br},$$
$$[\text{Pt}(\text{CH}_3)_3(\text{NH}_3)_3]\text{Cl}, [\text{Pt}(\text{CH}_3)_3\text{Py}_2\text{Cl}], [\text{Pt}(\text{CH}_3)_3\text{PyNH}_3\text{Z}].$$

A new synthesis of $(\text{CH}_3)_3\text{PtJ}$ was carried out by a reaction
of CH_3MgJ in benzene-ether solution with $\text{K}[\text{PtC}_3\text{H}_6\text{Cl}_3]$,
 $\text{K}_2[\text{PtCl}_6]$ and dehydrated Na_2PtCl_6 .

The best yield of $(\text{CH}_3)_3\text{PtJ}$ - approximately 55 %, was

Card 1/2

On the Amino Derivatives of Trimethyl Platinum

78-3-6-9/30

obtained with $(\text{Na}_2)_2[\text{PtCl}_6]$. Due to the determination of the molecular weight of the compounds

$[\text{Pt}(\text{CH}_3)_3 \cdot \text{PyJ}]$ and $[\text{Pt}(\text{CH}_3)_3 \cdot (\text{NH}_3)_2 \text{J}]$

it was found that these compounds are monomeric. The reactions of trimethyl platinum compounds investigated show that the methyl group is immovable in these compounds. However, the amino group in the compounds of type $[\text{Pt}(\text{CH}_3)_3 \cdot (\text{NH}_3)_3]_x$, on which occasion x represents J, Br or Cl, shows various mobility in dependence on the halide ion.

In the interaction of diamine- $[\text{Pt}(\text{CH}_3)_3 \cdot (\text{NH}_3)_2 \cdot \text{J}]$ with pyridine only one NH_3 group from the inner sphere of the complex can be exchanged by Py, namely under the formation of trimethyl amino pyridine iodine platinum

$([\text{Pt}(\text{CH}_3)_3 \cdot \text{NH}_3 \cdot \text{PyJ}])$.

There are 1 figure, 2 tables, and 14 references, 5 of which are Soviet.

Card 2/3

On the Amino Derivatives of Trimethyl Platinum

ADDITIONAL: Institut obshcheni organicheskoy khimii im.
N. N. Semenova (Moscow) Institute of General and Inorganic
Chemistry (Moscow) (USSR) (part of the USSR)

SUBMISSION: May 21, 1962

AVAILABLE: Current literature

1. Trimethyl platinum--Properties 2. Amino derivatives--Synthesis

Card 5/3

70-3-4-25/38

AUTHORS: Moskvin, A. I., Gel'man, A. D.

TITLE: Determination of the Composition and Instability Constants of Oxalate- and Carbonate Complexes of Plutonium-IV (Opredeleniye sostava i konstant nestoykosti oksalatnykh i karbonatnykh kompleksov plutoniya (IV))

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 4, pp. 962-974
(USSR)ABSTRACT: The solubility of $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{H}_2\text{O}$ in solutions of ammonium oxalate of concentrations of from 0,001 - 0,35 mol/l in the presence of 1 mol HNO_3 were determined. Based on the achieved results the composition of the complexes as well as the stability of the oxalate complexes of Pu-IV were determined. For $[\text{Pu}(\text{C}_2\text{O}_4)]^{2+}$ $K_H = 1,8 \cdot 10^{-9}$, for $[\text{Pu}(\text{C}_2\text{O}_4)_2]^0 = 1,2 \cdot 10^{-17}$, for $[\text{Pu}(\text{C}_2\text{O}_4)_3]^{2-} = 4,0 \cdot 10^{-24}$, for $[\text{Pu}(\text{C}_2\text{O}_4)_4]^{4-} = 3,2 \cdot 10^{-28}$.The solubility of plutonium-IV-hydroxide at constant ion-density in aqueous solutions of K_2CO_3 0,36-3,62 mol/l and at

Card 1/3

78-3-4-25/38

Determination of the Composition and Instability Constants of Oxalate-
and Carbonate Complexes of Plutonium-IV

a temperature of 20°C was determined. Also the solubility of plutonium-IV-hydroxide in aqueous solutions of K_2CO_3 of various concentrations without constant ion-density was determined. It was found that with an increase of the concentration of K_2CO_3 the solubility of plutonium-IV-hydroxide increases under the formation of complexes of Pu-IV-carbonate. The carbonate complex of plutonium-IV has the following composition: $[Pu(CO_3)]^{2+}$ with an instability constant of

$1,1 \cdot 10^{-47}$.

With carbonate complex solutions of plutonium-IV also the absorption spectrum was determined and the existence of the carbonate complex was proved by that. The formation of plutonium-IV-carbonate complexes proceeds stepwise. In solutions there exist several plutonium-IV-carbonate solutions of various compositions. The tendency of plutonium of other valence to form complexes with oxalation was also investigated. The tendency to complex formation of plutonium has the following order: $Pu^{4+} > Pu^{3+} > Pu^{3+} > PuO_2^{2+} > PuO_2^+$.

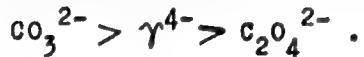
Card 2/3

78-3-4-25/38

Determination of the Composition and Instability Constants of Oxalate- and Carbonate Complexes of Plutonium-IV

The tendency of plutonium to form complexes with different anions CO_3^{2-} , $\text{C}_6\text{H}_5\text{O}_7^{3-}$, $\text{C}_4\text{H}_4\text{O}_6^{2-}$ has probably the same order as with oxalates.

Based on the instability constant of plutonium-IV with some complex partners the tendency to form complexes of Pu-IV-ions can be classified as follows:



γ^{4-} - anion of ethylene-diamine tetraacetic acid.

There are 5 figures, 7 tables, and 14 references, 11 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
(Institute for Physical Chemistry, AS USSR)

SUBMITTED: July 27, 1957

Card 3 /3

Gel'man, A. D.

AUTHORS: Gel'man, A. D., Sokhina, L. P. 76-3-5-8/39

TITLE: Oxalate Complexes of Plutonium-(IV) (Oksalatnyye kompleksnyye soyedineniya plutoniya(IV))

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol 3, Nr 5, pp 1100-1104 (USSR)

ABSTRACT: The oxalate complexes of plutonium-(IV) in solid phase have been isolated and their properties were examined in detail. $(\text{NH}_4)_6[\text{Pu}(\text{C}_2\text{O}_4)_5]$, $\text{Na}_4[\text{Pu}(\text{C}_2\text{O}_4)_4] \cdot 5\text{H}_2\text{O}$ were isolated as greenish yellow crystals. $\text{K}_4[\text{Pu}(\text{C}_2\text{O}_4)_4] \cdot 4\text{H}_2\text{O}$ and $\text{K}_6[\text{Pu}(\text{C}_2\text{O}_4)_5] \cdot 4\text{H}_2\text{O}$ were isolated and their existence proved by the determination of the electric conductivity. All plutonium compositions are soluble in water, and are stable in cold and in heat. By the increase of the pH -value of the oxalate complex, solutions decomposition occurs and hydroxides precipitate as final products. The oxalate solutions of plutonium-(IV) are also

Card 1/2

Oxalate Complexes of Plutonium-(IV)

78-3-5-8/39

decomposable by strong acidification.
The solid plutonium-(IV) oxalates modify if they are stored in air. This modification is connected with the destroying influence of α -rays upon the oxalate ion. By the influence of α -rays, the oxalate ion is decomposed into CO and CO_2 .
There are 6 tables and 3 references, 2 of which are Soviet.

SUBMITTED: November 15, 1957

AVAILABLE: Library of Congress

1. Plutonium oxalate--Properties

Card 2/2

GEL'MAN, A. D.

AUTHORS: Gel'man, A. D., Drabkina, L. Ye. 78-3-5-9/39

TITLE: Production and Examination of the Properties of Some
Oxalate Compounds of Hexavalent Plutonium (Poluchenije i
issledovaniye svoystv nekotorykh oksalatnykh soyedinenij
shestivalentnogo plutoniya)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol 3, Nr 5,
pp 1105-1108 (USSR)

ABSTRACT: Plutonium oxalate was produced and the composition was
found as $\text{PuO}_2(\text{C}_2\text{O}_4)_3\text{H}_2\text{O}$.
The precipitated plutonium is at first light pink, and
later changes into green.
The solubility of plutonyl-oxalate in nitric acid was
determined at different concentrations in the presence of
oxalic acid and ammonium oxalate. The solubility of
plutonyl oxalate in ammonium oxalate in presence of nitric
acid favors the assumption that, thereby, soluble plutonium-
-(IV)-oxalate complexes are formed. The composition of the
ammonium complex is represented by: $(\text{NH}_4)_2[\text{PuO}_2(\text{C}_2\text{O}_4)_2]$.
Card 1/2 In solutions of plutonyl oxalate in 1 n HNO_3 in presence

Production and Examination of the Properties of Some
Oxalate Compounds of Hexavalent Plutonium

78-3-5-9/39

of ammonium-oxalate, in addition, the following complexes
exist:

$[\text{PuO}_2\text{C}_2\text{O}_4]^0$ and $[\text{PuO}_2(\text{C}_2\text{O}_4)_2]^{2-}$ which have stability
constants of $2,2 \cdot 10^{-7}$ and $4,3 \cdot 10^{-12}$.

In aqueous solutions of ammonium- and potassium
oxalate, further complexes with a higher oxalate anion
content probably exist.

There are 2 figures, 4 tables, and 3 references, 2 of
which are Soviet.

SUBMITTED: November 15, 1957

AVAILABLE: Library of Congress

1. Plutonium oxalate--Properties
2. Complex compounds--Analysis
3. Ammonium oxalate--Chemical reactions

Card 2/2

AUTHORS: Gel'man, A. D., Zaytsev, L. M. 78-3-6-5/30

TITLE: Carbonate and Carbonate Oxalate Complexes of Plutonium-(IV)
I. Potassium Plutonium Carbonate (Karbonatnyye i karbonatno-
oksalatnyye kompleksnyye soedineniya plutoniya (IV) I.
Plutoniylkarbonaty kaliya)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 6,
pp. 1304-1311 (USSR)

ABSTRACT: The synthesis for the production of solid carbonate complex
compounds of plutonium-(IV) in greatest purity was elaborated.
Solid plutonium-(IV)-oxalate was dissolved in potassium-,
sodium-, and ammonia-carbonate as initial components. The
solid complex compounds were isolated by ethyl alcohol.
Also four carbonate complex compounds of plutonium-(IV) with
potassium were investigated and the following formulae were
determined for the compounds: $K_4[Pu(CO_3)_4] \cdot nH_2O$; $K_6[Pu(CO_3)_5] \cdot (3-4)H_2O$; $K_8[Pu(CO_3)_6] \cdot nH_2O$; $K_{12}[Pu(CO_3)_8] \cdot nH_2O$.
The microscopic investigations of the potassium carbonate
complex compounds of plutonium confirm the crystalline
structure of these compounds.

Card 1/2

Carbonate and Carbonate Oxalate Complexes of Plutonium-(IV) 78-3-6-5/30
I. Potassium Plutonium Carbonate

The investigations of the electric conductivity of the solutions show that the complex compound $K_{12}[Pu(CO_3)_8] \cdot nH_2O$ occurs in dissolved state. It was found that the coordination number of the plutonium carbonate complex compounds is 8. There are 8 tables and 15 references, 4 of which are Soviet.

SUBMITTED: November 15, 1957

AVAILABLE: Library of Congress

1. Plutonium compounds--Synthesis
2. Complex compounds--Production
3. Complex compounds--Synthesis

Card 2/2

AUTHORS:

Gel'man, A. D., Zaytsev, L. M.

SOV/78-3-7-15/44

TITLE:

II. Sodium Plutonylcarbonates (II. Plutoniylkarbonaty natriya)

PERIODICAL:

Zhurnal neorganicheskoy khimii, 1958, Vol. 3, Nr 7, pp:
1551-1554 (USSR)

ABSTRACT:

The sodium plutonylcarbonate complex was produced and the dependence between the concentration of the solvents and the composition of the obtained complex compounds was determined. The optimum conditions for the production are an 18-20% soda solution and alcohol of 55-60%. In the alcohol solution mentioned the sodium plutonylcarbonate compound has its lowest degree of solubility. By analysis of the solid phase it was found that the ratio Pu : CO₃ : Na is 1:4:4 and 1:5:6. Three sodium carbonate complex compounds of plutonium were prepared and investigated. The respective formulae are:
1. Na₄[Pu(CO₃)₄]₃H₂O; 2. Na₆[Pu(CO₃)₅]₂H₂O;
3. Na₆[Pu(CO₃)₅]₄H₂O.

In the course of the thermal decomposition of Na₄[Pu(CO₃)₄]₃H₂O

Card 1/2

II. Sodium Plutonylcarbonates

SOV/78-3-7-15/44

It was found that at 300-400°C 3 mol H₂O and 2 mol CO₂ are separated. The crystals retain their shape. The second compound produces large green crystals which, when being dehydrated, go over into a fine greenish-yellow crystal powder. The third compound is more stable. There are 3 figures and 3 tables.

SUBMITTED: November 15, 1957

1. Complex compounds--Solubility 2. Complex compounds--Chemical analysis 3. Complex compounds--Properties 4. Plutonium--Properties
Sodium--Properties

Card 2/2

AUTHORS: Gel'man, A.D., Zaytsev, L.M. 307/ 78-3-7-16/44

TITLE: III. Mixed Oxalate-Carbonate Compounds of Plutonium (IV)
(III. Smeshannyye oksalato-karbonatnyye soyedineniya
plutoniya (IV))

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 7, pp 1555-1564
(USSR)

ABSTRACT: Mixed oxalate-carbonate compounds of plutonium (IV) were synthesized and investigated. The following compounds were produced: $K_2[Pu(CO_3)_2C_2O_4] \cdot nH_2O$; $Na_4[Pu(CO_3)_2(C_2O_4)_2] \cdot 3H_2O$; $Na_4[Pu(CO_3)_3 \cdot (C_2O_4)] \cdot nH_2O$; $K_4[Pu(CO_3)_3 \cdot C_2O_4] \cdot nH_2O$; $K_6[Pu(C_2O_4)_3 \cdot C_2O_4] \cdot nH_2O$; $K_{10}[Pu(C_2O_4)_4(C_2O_4)_3] \cdot nH_2O$; $K_{12}[Pu(CO_3)(C_2O_4)_7] \cdot nH_2O$. By crystal optics and X-ray analysis it is shown that the production and composition of the aforementioned complex compounds depend on the concentration of the sodium carbonate. The complex compounds existing in the solution depend on the concentration of the oxalate- and carbonate ions. It is shown that in the

Card 1/2

III. Mixed Oxalate-Carbonate Compounds of
Plutonium (IV)

30V/ 78-3-7-16/44

solution complicated complex compounds occur which decompose
with separation of the solid phase.

The aqueous solutions are unstable. As a result of the decomposition of the complexes plutonium-hydroxide is precipitated. Several problems connected with the structure of the products investigated are explained. There are 16 tables.

SUBMITTED: November 15, 1957

1. Complex compounds--Synthesis
2. Complex compounds--Chemical analysis
3. Complex compounds--Properties
4. Plutonium hydroxide--Precipitation

Card 2/2

SOV/78-3-0-34/48

AUTHORS: Drabkina, L. Ye., Moskvin, A. I., Gel'man, A. B.

TITLE: Determination of the Solubility Product of Plutonyl-Oxalate
(Opredeleniye proizvedeniya rastvorimosti plutoniloksalata)PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol. 3, Nr 9, pp. 1934-
1936 (USSR)ABSTRACT: The solubility product was determined of plutonyl oxalate in
1,1, 2,0, 3,08 mol. HNO_3 and in mixtures of $\text{HNO}_3\text{-H}_2\text{C}_2\text{O}_4$. The
solubility product of plutonyl oxalate has an average value
of $6,0 \cdot 10^{-10}$. With an increase of the oxalic acid concentration
the solubility of plutonyl oxalate decreases. Approximate
values of the solubility product of plutonyl oxalate were also
determined by means of the graphical method from data on the
solubility of plutonyl oxalate in mixed solutions of
 $\text{HNO}_3\text{-(NH}_4\text{)}_2\text{C}_2\text{O}_4$. The solubility product, determined by the
graphical method, amounts to $1,4 \cdot 10^{-10}$. This value corresponds
quite well to the value found in the experimental way. There
are 1 figure, 2 tables, and 10 references, 9 of which are

Card 1/2

SOV/78-3-8-34/48

Determination of the Solubility Product of Plutonyl Oxalate

Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of
Physical Chemistry, AS USSR)

SUBMITTED: October 31, 1957

Card 2/2

GEL'MAN, A.D.

89-3-5/30

AUTHORS: Gel'man, A. D., Mefod'yeva, M. P.

TITLE: The Reduction of Neptunium to the Trivalent State by a Chemical Method (O vosstanovlenii neptuniya do trekhvaientnogo sostoyaniya khimicheskim metodom)

PERIODICAL: Atomnaya Energiya, 1958, Vol. 4, Nr 3, pp. 271 - 274 (USSR)

ABSTRACT: By means of the spectrographic method it was found that in a 1 to 1,5 M nitric acid and hydrochloric acid solution of rongalite ($\text{NaHSO}_3 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$), neptunium (IV) is reduced to Np(III). The reduction takes place in nitrogen atmosphere as well as in air. The degree of reduction as well as the stability of Np(III) are, however, remarkably increased in a nitrogen atmosphere. It was found that by an increase of the general content of the reducing agent in the solution (hydrasin + rongalite) the reduction to Np(III) is favored. The reduction of neptunium is on the average accomplished to 70 % in nitric acid solution but to 95 % in hydrochloric acid solution. It was further found that in the reduction of Np(V) in ron-

Card 1/2

89-3-5/30

The Reduction of Neptunium to the Trivalent State by a Chemical Method

galite a mixture of Np(III) + Np(IV) is formed. Np(III) shows a considerable stability against oxidation by atmospheric oxygen in the mixture of Np(IV) with Np(III). There are 4 figures, and 4 references, 1 of which is Slavic.

SUBMITTED: January 19, 1957

AVAILABLE: Library of Congress

1. Neptunium-Reduction 2. Spectrographic method-Application

/
Card 2/2

AUTHORS:

Gel'man, A. D., Moskvin, A. I.

20-3-21/59

TITLE:

An Investigation of the Complex Oxalates and Carbonates of Plutonium ^{IV} in Water Solutions by Means of the Solubility Method (Issledovaniye oksalatnykh i karboratnykh kompleksov plutoniya (IV) v vodnykh rastvorakh metodom rastvorimosti).

PERIODICAL:

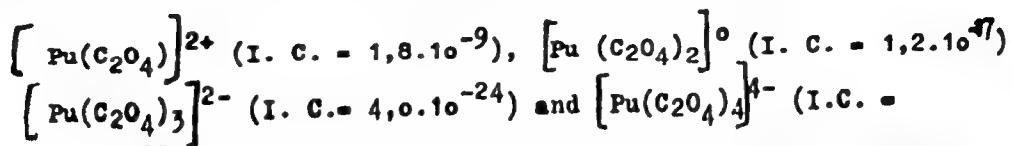
Doklady AN SSSR, 1958, Vol. 118, Nr 3, pp. 493-496 (USSR)

ABSTRACT:

No date can be found in publications concerning the composition and stability of the carbonates complex of plutonium (IV). In this work the authors give the determination of the composition as well as of the instability constants of Pu (IV) as mentioned in the title. 4-6 hours are sufficient to reach the equilibrium between the ammonium-oxalate solution and the solid phase of Pu (IV) oxalate at $20 \pm 0,02^\circ$. The experimental results are mentioned in table 1. The solubility of Pu (IV) oxalate decreases with the increase of the concentration of ammonium-oxalate from 0,001 to 0,005 Mol/liter, it reaches a minimum of $3,55 \cdot 10^{-5}$ mol. Pu(IV) per liter and then increases because of the complex formation of Pu(IV) with oxalations. The solubility is expressed by means of an equation (1). Complex ions with general instability constants (= I. C. in brackets) are formed:

Card 1/3

An Investigation of the Complex Oxalates and Carbonates of Plutonium ^{20-3-21/59} /IV/ in Water Solutions by Means of the Solubility Method.



$\sim 3,3 \cdot 10^{-28}$). These constants correspond to a complete decomposition of the ions of Pu(IV). From these general instability constants the stepwise constants were determined. Both kinds of constants correspond to different decomposition schemes (2) and (3). Table 2 gives the solubility of Pu(IV)-oxalate in water and in H_2SO_4 , HNO_3 and HClO_4 . From this follows that the solubility, but that then, starting from 0,1 N, it increases again. Because of their interaction with the oxalate in aqueous solutions the acids form a series: $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HClO}_4$. The pH of a saturated Pu(IV) oxalate solution was equal to 4,4, the molecular electric conductivity $470 \Omega^{-1}$. The dissociation process of Pu(IV) oxalate is explained by means of a scheme for its analogy with U^{4+} . The estimated constant of the acid dissociation of Pu(IV) gave $\sim 3 \cdot 10^{-5}$. Furtheron the solubility of Pu(IV) oxalate in a mixed solution $\text{HNO}_3 - (\text{NH}_4)_2\text{C}_2\text{O}_4$ (table 1), as well as of Pu(IV) hydroxide in K_2CO_3 , with a constant ionic density with an addition of HCl and KClO_4 (table 3) are measured. From tabl. 3 it

Card 2/3

An Investigation of the Complex Oxalates and Carbonates of Plutonium /IV/ in Water Solutions by Means of the Solubility Method. 20-3-21/59

can be seen that the solubility of the hydroxide increases with the increasing K_2CO_3 concentration because of the complex formation of Pu(IV) with Carbonate ions. The complex ion $[Pu(CO_3)]^{2+}$ has an instability coefficient of the concentration $1,1 \cdot 10^{-47}$. Absorption spectra of the solutions of the latter complex were investigated. Table 4 gives the calculated values of the ion potential. From this is seen the tendency for complex formation of single plutonium ions: $Pu^{4+} \rightleftharpoons Pu^{3+} \rightleftharpoons PuO_2^{2+} \rightleftharpoons PuO_2^{2-}$, which decreases with the decreases of the ion potential. By means of the data in table 5 the anions can be arranged in a series according to their tendency for complex formation with Pu(IV): $CO_3^{2-} \rightleftharpoons C_4H_4O_2^{-} \rightleftharpoons C_6H_5O_3^{-} \rightleftharpoons C_2O_4^{2-}$. There are 5 tables, 5 references, 4 of which are Slavic.

ASSOCIATION: Institute for Physical Chemistry AN USSR (Institut fizicheskoy khimii Akademii nauk SSSR).

PRESENTED: August 15, 1957, by I. I. Chernyayev, Academician

SUBMITTED: August 1, 1957

AVAILABLE: Library of Congress

Card 3/3

SOV/20-120-1-25/63

AUTHORS: Artyukhin, P. I., Gel'man, A. D., Medvedovskiy, V. I.

TITLE: Investigation of the Redox Potentials of Plutonium in Nitric Acid (Issledovaniye okislitel'no-vosstanovitel'nykh potentsialov plutoniya v azotnoy kisloty)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 1, pp. 98-100 (USSR)

ABSTRACT: The authors determined the formal redox potentials of various plutonium pairs in nitric acid solutions of different concentrations, as well as the disproportionating of Pu (IV) in nitric acid solutions. The potentials of the pair Pu(IV) - Pu(III) were measured at 25° in a carefully purified nitrogen atmosphere by means of an apparatus already described earlier (Ref 10). These measurements were carried out within the whole range of the ratios of the concentrations of Pu(IV) and Pu(III). The experiments of the direct determination of the potentials of the pairs Pu(VI) - Pu(IV) did not turn out to be successful. The measurement of the formal potentials of the pair Pu(VI) - Pu (IV) was carried out by

Card 1/3

30V20-120-1-25/63
Investigation of the Redox Potentials of Plutonium in Nitric Acid

disproportionating of Pu(IV) at low concentrations of nitric acid. This disproportionating of Pu(IV) was carried out at 25°. From the redox potentials measured on conditions of equilibrium and from the values of equilibrium concentrations the formal potentials for the pairs Pu(IV) - Pu(III), Pu(VI) - Pu(IV) and Pu(VI) - Pu(III) are calculated and given in a table. The formal potentials of the pairs Pu(VI) - Pu(IV), Pu(VI) - Pu(III) highly increase with increasing concentration of the hydrogen ions. The potentials of these pairs depend as the fourth power on the concentrations of the ions H⁺. The reactions taking place at the electrode are written down. Using these equations the formal potentials of the pairs Pu(VI) - Pu(IV) and Pu(VI) - Pu(III) in 1 N HNO₃ are calculated. The results obtained agree well with those of other authors. Proceeding from the discussed considerations schemes for the formal potentials of plutonium in nitric acid solutions are proposed and given. A diagram shows the changes of the concentrations of Pu(III), Pu(IV) and Pu(VI) with progressing time in 0,40 N HNO₃. In spite of the existing complex formation of Pu(IV) the constants of the velocity of the disproportionating of Pu(IV) in nitric acid

Card 2/3

SOV/20-120-1-25/63

Investigation of the Redox Potentials of Plutonium in Nitric Acid

obtained are the same as in hydrochloric acid. There are 1 figure, 3 tables, and 15 references, 3 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
(Institute of Physical Chemistry AS USSR)

PRESENTED: December 24, 1957, by I. I. Chernyayev, Member, Academy of Sciences, USSR

SUBMITTED: December 24, 1957

- 1. Plutonium--Analysis
- 2. Oxidation-reduction reactions
- 3. Nitric acid--Applications

Card 3/3

AUTHORS: Gel'man, A.D., Drabkina, L.Ye., Moskvin, A.I. SUV/78-3-7-14/44

TITLE: The Determination of the Composition and of the Instability Constants of the Oxalate Complex Ions of Plutonium (VI)
(Oprydeleniye sostava i konstant nestoykosti oksalatnykh kompleksov ionov plutoniya (VI))

PERIODICAL: Zhurnal neorganicheskoy khimi, 1958, Vol 3, Nr 7, pp 1546-1550
(USSR)

ABSTRACT: In the present paper the results obtained in connection with the determination of the composition and the instability constants of oxalate complexes of PuO_2^{2+} by the solubility of plutonium (VI) oxalate in HNO_3 in the presence of ammonium oxalate are given. The determination of the solubility of plutonyl oxalate in nitric acid in the presence of ammonium oxalate was carried out at 20°C , and a value of $(3.3 \cdot 10^{-3} \text{ mol/l})$ plutonyl oxalate was obtained. Solubility increases with an increase of the ammonium oxalate concentration because complexes are formed. The solubility product of $\text{PuO}_2 \cdot \text{C}_2\text{O}_4 \cdot 3 \text{H}_2\text{O} \approx (5.9) \cdot 10^{-10}$.

Card 1/2

The Determination of the Composition and of the Instability 30/78-3-7-14/44
Constants of the Oxalate Complex Ions of Plutonium (VI)

In oxalate solutions of plutonium (VI) the following complexes exist: $[\text{PuO}_2\text{C}_2\text{O}_4]^0$ and $[\text{PuO}_2(\text{C}_2\text{O}_4)_2]^{2-}$. Their instability constants are: (2.0 ± 0.7) and $(3.4 \pm 4.3) \times 10^{-12}$ respectively. There are 1 figures, 1 table, and 5 references, 4 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii, Akademii nauk SSSR (Institute of Physical Chemistry, AS USSR)

SUBMITTED: October 31, 1957

- 1. Complex ions--Stability
- 2. Complex ions--Solubility
- 3. Ammonium oxalate--Applications

Card 2/2

SOV/78-3-12-11/36

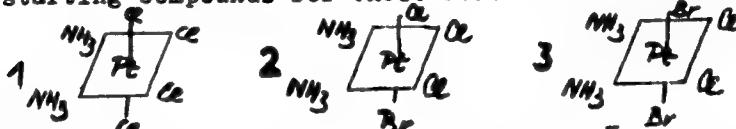
AUTHORS: Eessen, L. N., Zakharova, F. A., Gel'man, A. D.TITLE: Concerning the Synthesis of Isomers With Six Different Addenda
(K sintezu i somerov s shest'yu razlichnymi zamestitelyami)PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 12,
pp 2654-2661 (USSR)ABSTRACT: $[\text{PyNH}_3\text{BrNO}_2\text{ClJPt}]$ and $[\text{PyClNH}_3\text{NO}_2\text{BrJPt}]$, two geometric isomers with six different addenda, were synthesized. The starting material for the synthesis of the trans isomers was $[\text{PyNH}_3\text{BrNO}_2\text{Pt}]$, containing divalent platinum. The compound was first treated with NaNO_2 , then with chlorine, and finally converted to the trans form $[\text{PyNH}_3\text{BrNO}_2\text{ClJPt}]$ by treating with potassium iodide. This product has a dark green color, and has a solubility in water of 0.05 grams per 100 grams solution. A decomposition with the generation of iodine takes place at 200° when it is heated in open capillary tubes. The synthesis of the cis isomer $[\text{PyClNH}_3\text{NO}_2\text{BrJPt}]$ was carried out using the salt

Card 1/4

SOV/78-3-12-11/36

Concerning the Synthesis of Isomers With Six Different Addenda

$K[\text{PtPyCl}_3]$. At 40-60°C in aqueous solution the NO_2 group containing an equivalent amount of sodium nitrite was added to the salt. The compound was then oxidized with bromine and the produced salt converted to the cis isomer with six addenda by reaction with potassium iodide. The cis isomer is a fine crystalline powder with a dark brown color, and melts without decomposition at 200°C. It has a solubility in water at 25° of 0.095 grams per 100 grams solution. The syntheses of isomers with two, three, and eight addenda were not successful, because the addition of the NO_2 group to the tetravalent platinum compound is extremely complicated. A few exchange reactions involving simple platinum (IV) compounds were carried out. The starting compounds for these reactions were the following:



By reacting potassium bromide with the $[(\text{NH}_3\text{Cl})_2\text{Cl}_2\text{Pt}]$ salt in the ratio 1:1 the displacement of one chlorine in the co-

Card 2/4

SOV/78-3-12-11/36

Concerning the Synthesis of Isomers With Six Different Addenda

ordinates Cl-Pt-Cl takes place. By reacting 2 moles of KBr with one mole of $[(\text{NH}_3\text{Cl})_2\text{Cl}_2\text{Pt}]$ an exchange of the two chlorine atoms with bromine takes place under development of $[(\text{NH}_3\text{Cl})_2\text{Br}_2\text{Pt}]$. The bromine ion in the coordinates Br-Pt-Br could not be displaced by reaction with KCl. The experimental results show that chlorine and bromine have different coordination affinities in the inner spheres of tetravalent platinum compounds. An exchange of chlorine and bromine with the NO_2 group in the coordinates Br-Pt-Br, Br-Pt-Cl, and Cl-Pt-Cl did not occur. The course of the exchange reactions in the inner spheres of tetravalent platinum compounds is dependent upon the various coordination mobilities of the addenda. There are 11 Soviet references.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences, USSR)

Card 3/4 .

SOV/78-3-12-11/36

Concerning the Synthesis of Isomers With Six Different Addenda

SUBMITTED: August 5, 1957

Card 4/4

GEL'MAN, A. D.

AUTHORS:

Gel'man, A. D., Matorina, N. N., Moskvin, A. I. 89-1-6/29

TITLE:

The Determination of the Composition and the Instability Constant of Oxalate Complexes of Pu⁴⁺ Compounds by the Method of Ion Exchange
(Opravleniye sestava i konstant nestoykosti oksalatnykh kompleksov
soyedinneniya Pu⁴⁺ metodom ionnogo obmena).

PERIODICAL:

Aтомная Энергия, 1958, Vol. 4, Nr 1, pp. 52 - 56 (USSR).

ABSTRACT:

By the method of ion exchange the formation of ion complexes of Pu⁴⁺ in oxalate solutions was determined, and the pH value of the solutions was found to fluctuate between 1,4 and 2,8. Measuring results:
1.) The instability constant of the complex ion $[\text{Pu}(\text{C}_2\text{O}_4)_2]^-$ is practically constant with in the range of the pH values from 1,47 to 2,65 (11 values).
2.) In a solution with $\text{pH} > 1,7$ a mixture of complex ions $[\text{Pu}(\text{C}_2\text{O}_4)_2]^-$ and $[\text{Pu}(\text{HC}_2\text{O}_4)_4]^-$ is developed, and the average instability constants for these two types of ions were measured to be $K'_{\text{H}} = 7,1 \cdot 10^{-10}$ and $K'' = 1,1 \cdot 10^{-11}$.

Card 1/2 3.) The constants K'_{H} and K''_{H} correspond to a total decay of the

Card 2/2

GEL'MAN A. D.

5(4)

AUTHORS: Babushkin, A. A., Gribov, L. A.,
Gel'man, A. D.

SOV/20-123-3-22/54

TITLE: The Nature of the Bond Between the Central Atom and Some
Unsaturated Molecules in Complex Platinum Compounds (O
kharaktere svyazi mezhdu tsentral'nym atomom i nekotoryimi
nenasyshchennymi molekulami v kompleksnykh soyedineniyakh
platiny)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 3,
pp 461-463 (USSR)

ABSTRACT: The problem of the bond between metal~~s~~ and the molecule
mentioned in the title was investigated in numerous papers.
A respective survey is given in reference 1. According to
A. D. Gel'man (Ref 2) the platinum atom represents at the
same time an electron donor and acceptor. In consequence of this
a covalent double bond results between the central atom and
the olefin. Chatt and Duncanson (Ref 4) suggest a scheme for
this bond which can be regarded as π -electron interaction.
The authors do not agree to the interpretation of the spectra
observed. Chatt and Duncanson (and Ref 5, according to them)
conclude from their interpretation that the double bond of the

Card 1/4

The Nature of the Bond Between the Central Atom
and Some Unsaturated Molecules in Complex Platinum Compounds

SOV/20-123-3-22/54

olefin is maintained also in the complex formation. The authors state, however, that the reasons for this fact are not sufficient. The purpose of their paper was therefore to perform a critical analysis of the infrared spectra of complex platinum compounds with ethylene, propylene and carbon monoxide: 1) contrary to reference 4, the frequencies in the range above 3000 cm^{-1} are a necessary but by no means sufficient proof of the maintenance of the double bond C—C in the olefin part of the complex. Due to the similarity of the electron configuration in the CH_2 -group of the ethylene, ethylene oxide and cyclopropane molecules the authors suppose that the olefin is forming with platinum a compound according to the type of a triangular cyclic structure. 2) According to the above-mentioned statements it is more correct to attribute the frequencies of the ethylene and propylene complexes with platinum in the range $1490-1510\text{ cm}^{-1}$ to the deformation oscillation CH_2 (Ref 7a), but not to the frequency of valence oscillations of the double bond C—C. 3) The frequency of the non-plane

Card 2/4

The Nature of the Bond Between the Central Atom
and Some Unsaturated Molecules in Complex Platinum Compounds

SOV/20-123-3-22/54

deformation oscillations of the CH₂-group is a typical feature of olefins (Ref 8). The absence of this frequency in the complex compound under consideration and the presence of 4 additional intense frequencies between 1300 and 700 cm⁻¹ (as compared with the spectra of the initial addenda) proves a considerable transformation of the ethylene molecule that must be related with the transformation of the double bond C=C into a single one. 4) The above-mentioned considerations are in accordance with the data on the structure of the complex compound mentioned (Ref 9). According to these data, the ethylene molecule is vertical to the PtCl₃-plane and, shows with respect to the latter, nearly a symmetric position. The distance between the carbon atoms d = 1.50 Å is a value characteristic of a single bond between these atoms. 5) The analysis of the infrared spectrum of the complex compound proves that the double bond C=C in ethylene is transformed into a single one on the entrance of the platinum atom into the inner sphere. Therein the strength of the bond between

Card 5/4

The Nature of the Bond Between the Central Atom
and Some Unsaturated Molecules in Complex Platinum Compounds

SOV/20-123-3-22/54

platinum and the carbon atoms is according to the order
of magnitude of the strength identical with an ordinary
covalent bond. 6) The statements made in points 1-3 are
valid both for $K[PtC_2H_4Cl_3]H_2O$ and $K[PtC_3H_6Cl_3] \cdot H_2O$.

For this reason the authors claim that the structure and
nature of the formation of the propylene bond with the
central atom are similar to those of ethylene with platinum.
There are 10 references, 5 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute
of Physical Chemistry of the Academy of Sciences USSR)

PRESENTED: July 7, 1958, by V. I. Spitsyn, Academician

SUBMITTED: June 26, 1958

Card 4/4

5(4), 21(1)

AUTHORS:

Gel'man, A. D., Artyukhin, P. I., Moskvin, A. I.

SOV/78-4-6-19/44

TITLE:

Investigation of the Complex Formation of Pentavalent Plutonium in Ethylene-diamine-tetraacetic Acid by the Ion Exchange Method
(Issledovaniye kompleksobrazovaniya pyativalentnogo plutoniya v etilendiamintetraatsetatnykh rastvorakh metodom ionnogo obmena)PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 6, pp 1332-1335
(USSR)

ABSTRACT:

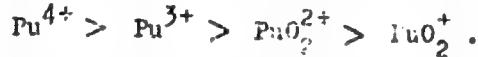
The complex formation process of $\text{Pu}^{(V)}$ in ethylene-diamine-tetraacetic acid was investigated by the ion exchange method. The results of the distribution of the pentavalent plutonium between 0.05 mol-solution NH_4Cl and the cation exchangerwith different pH-value are given in table 1. They show that the complex ion PuO_2Y^3- is produced in the pH-range 4 - 5with the instability constant $6.2 \cdot 10^{-11}$. The influence of the pH-value on the distribution of $\text{Pu}^{(V)}$ between 0.05 mol solution NH_4Cl and the ion exchanger in the case of presence and

absence of Komplexon is given in figure 1. The instability

Card 1/2

SOV/70-4-6-19/44
Investigation of the Complex Formation of Pentavalent Plutonium in Ethylene-diamine-tetraacetic Acid by the Ion Exchange Method

constants of the ADTA-complex ions of Pu(III), Pu(VI) and Pu(V) were compared and given in table 3. The inclination of different plutonium ions to complex formation has the following series:



The Pu(IV)-ion and the smallest Pu(7)-ion are most inclined to complex formation with the anion Y^{3+} . There are 2 figures, 3 tables, and 7 references, 4 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
(Institute of Physical Chemistry of the Academy of Sciences,
USSR)

SUBMITTED: April 16, 1958

Card 2/2

5(2) 5.2200 (A)

66298
SOV/78-4-12-6/35AUTHORS: Gel'man, A. D., Zaytsev, L. M.

TITLE: Simple and Complex Carbonate Compounds of Plutonium (IV)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 12,
pp 2688-2696 (USSR)

ABSTRACT: In an earlier paper (Ref 3) the authors reported on potassium- and sodium-plutonium carbonates. The present article treats of the corresponding complex ammonia compounds of tetravalent Pu. The soluble carbonate complexes of Pu(IV) were obtained by reducing the Pu(VI) tricarbonate with H_2O_2 in 10% ammonium carbonate solution. When pouring the solution into 75-80% methyl- or ethyl alcohol the green complex was precipitated in the form of sirup and could be dried by decantation and washing with absolute alcohol. Complete dehydration failed as decomposition occurred. The analysis had therefore to be made by means of an aqueous substance. It showed the composition $(NH_4)_6[Pu(CO_3)_5]nH_2O$. Storing in alcohol for some time or drying in air effected decomposition with brown coloring. Thermal analysis of the decomposed product indicated the absence of hydroxyl groups so that the composition of $PuO_2 \cdot PuOCO_3 \cdot 3H_2O$ was

Card 1/3

66298

SOV/78-4-12-6/35

Simple and Complex Carbonate Compounds of Plutonium (IV)

ascribed to it. To prevent rapid decomposition of the green complex salt, it was stored in the desiccator in the presence of ammonium carbonate and thus only partially decomposed to form the compound $(\text{NH}_4)_4[\text{Pu}(\text{CO}_3)_4] \cdot n\text{H}_2\text{O}$. When the hexavalent Pu compound is reduced in ammonium carbonate solution of high concentration (30% at 35°), the compound $(\text{NH}_4)_8[\text{Pu}(\text{CO}_3)_6] \cdot n\text{H}_2\text{O}$ is formed, which is also green. All of the three resulting complex compounds form green solutions in water, which decompose after a few minutes to separate green amorphous plutonium hydroxide. When studying the compound $(\text{NH}_4)_4[\text{Pu}(\text{CO}_3)_4] \cdot 4\text{H}_2\text{O}$ it was found that the change in the pH of its aqueous solution sets in only after 5-8 min. Meanwhile it was possible to measure the apparent molecular weight and electrical conductivity. The complex dissociated to form 5 ions, the apparent molecular weight being 113.0. Since the calculated molecular weight is 623, this dissociation was confirmed. The deviation (623 : 113 ≈ 5.5) is caused by the beginning decomposition. The complex compounds can be longer stored in ammonium carbonate solutions than in pure water. Thermal analysis was carried out at low temperature

Card 2/3

4

66298

SOV/78-4-12-6/35

Simple and Complex Carbonate Compounds of Plutonium (IV)

according to G. G. Tsurinov's method (Ref 4). The compound $(\text{NH}_4)_6[\text{Pu}(\text{CO}_3)_5] \cdot n\text{H}_2\text{O}$ splits off one ammonium carbonate molecule at 58° . Partial dehydration occurs at 70° . At 80° the compound $(\text{NH}_4)_4[\text{Pu}(\text{CO}_3)_4] \cdot 4\text{H}_2\text{O}$ decomposes to form $\text{PuO}_2 \cdot \text{PuOCO}_3$, and at 110° the basic oxycarbonate decomposes to yield PuO_2 . The slow decomposition of plutonium tetracarbonate in the air, however, leads to the compound $\text{PuOCO}_3 \cdot 2\text{H}_2\text{O}$. When heating the solutions of the Pu complex compounds, the compound $2.5\text{PuO}_2 \cdot \text{PuOCO}_3 \cdot 5.5\text{H}_2\text{O}$ is precipitated. The normal plutonium carbonate $\text{Pu}(\text{CO}_3)_2 \cdot n\text{H}_2\text{O}$ could not be obtained. There are 4 figures, 10 tables, and 4 references, 3 of which are Soviet.

SUBMITTED: September 9, 1958

4

Card 3/3

5(2) 21(1)

SOV/89-7-2-11/24

AUTHORS: Gel'man, A. D., Moskvin, A. I., Artyukhin, P. I.

TITLE: The Compositions and Dissociation Constants of Pu(V) and Pu(III) Complexes with Ethylenediaminetetraacetic Acid (sostav i konstanty dissotsiatsii kompleksov Pu(V) i Pu(III) s etilendiamintetraakusnoy kislotoy)

PERIODICAL: Atomnaya energiya, 1959, Vol 7, Nr 2, pp 162 - 163 (USSR)

ABSTRACT: The complex formation of Pu(V) with and without complex-forming ethylene diamine tetra acetic acid (EDTA) was measured with the ion exchange method under the following conditions: KU-2; pH range 3.3 to 5.1; ionic force $\mu = 0.05$ (0.05 M NH_4Cl solution); temperature $20 \pm 1^\circ\text{C}$. In the examined pH range a complex ion of the type $\text{PuO}_2\text{Y}^{3-}$ (Y^{4-} - anion of the EDTA) is formed with a dissociation constant $K = 6.8 \cdot 10^{-11}$. Similarly the complex formation was determined for Pu(III) in the pH range 1.2 to 3.4, in a nitrogen atmosphere $\mu = 1$ (1 M NH_4Cl). The following complex ions are formed: PuY^- and PuHY ; their dissociation constants are $4.4 \cdot 10^{-18}$ and $6.2 \cdot 10^{-10}$. By this and earlier data the dissociation constants of the EDTA complexes of the

Card 1/2

The Compositions and Dissociation Constants of Pu(V) and SOV/89-7-2-11/22
Pu(III) Complexes with Ethylenediaminetetraacetic Acid

trivalent transuranic elements (Pu-Cf) can be compared and one may see that with increase of the Z the strength of the complexes of the type MY^- increases, which is easy to understand because of the increase of the ion potential. When the dissociation constants of the complex plutonium ions are being compared it can be established that the tendency of complex formation decreases in the following sequence:

$Pu^{4+} > Pu^{3+} > PuO_2^{2+} > PuO_2^+$, i. e. with decrease of the ion potential.
There are 1 table and 6 references, 4 of which are Soviet.

SUBMITTED: January 6, 1959

Card 2/2

5(2, 3)

AUTHORS:

Gel'man, A. D., Mefod'yeva, M. P.

SOV/20-124-4-24/67

TITLE:

On the Complex Formation of Np^{4+} and NpO_2^+ With Trilon B
in Aqueous Solutions (O kompleksosobrazovanií Np^{4+} i NpO_2^+ s
trilonom B v vodnykh rastvorakh)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124. Nr 4,
pp 815-818 (USSR)

ABSTRACT:

In spite of several investigations of the interaction of actinides with Trilon B (disodium salt of ethylene diamine tetraacetic acid) there are no data in publications available on the subject under review. The authors tried to fill the gap. A. Complex formation of Np with trilon B.

Addition of excess Trilon B to the $\text{Np}(\text{IV})$ -solution at pH 5.5 shifts the absorption intensity toward the long-wave range; instead of a maximum 722 $\text{m}\mu$, 740 $\text{m}\mu$ appears and a second one at 780 $\text{m}\mu$. The maximum 960 $\text{m}\mu$ is shifted up to 983 $\text{m}\mu$. pH increase up to 6.8 leads to a reduction of the maxima 740 and 780 $\text{m}\mu$ with time, while instead of 983 a maximum

Card 1/5

SOV/20-124-4-24/67

On the Complex Formation of Np^{4+} and NpO_2^{+} with
 Triton B in Aqueous Solutions

appears at 988 m^{u} . A decrease of the pH values down to
 5.2 and below led to a reverse process (Fig 1). On the
 curves of figure 2 2 horizontal sections (Plateaus) can be
 read: 1) between 0.5 n HCl and pH 2) from pH 3.5 to 6.5
 of the solution in which the complex formation was investigated.
 Apparently, only one single complex formation was investigated
 in each of both ranges. The composition, i. e. the ratio
 $[\text{Np}^{4+}]$ in the complex was determined by spectrophotometric
 titration of Np^{4+} solution with Triton (at constant acidity and
 $\mu = 1$). The authors calculated the stability constants for
 all complexes which could be produced within the system for
 (provided one of them is present at the respective moles).
 As follows from table 1, a stationary stability constant within
 the whole range of acidity is attained most favorably for
 $[\text{NpH}_3]^{3+}$ and $[\text{NpH}_2]^{2+}$. It is not possible to determine the
 presence of 2 different complexes according to experimental data.

Card 2/5